Monitoring for Microconstituents in an Advanced Wastewater Treatment (AWT) Facility and Modeling Discharge of Reclaimed Water to Surface Canals for Indirect Potable Use

Prepared by
Andrew Salveson, Jess Brown, Zhi Zhou
Carollo Engineers, P.C.
2700 Ygnacio Valley Road, Suite 300, Walnut Creek, CA 94598

Jose L. Lopez
South Florida Water Management District

Cosponsors:
United States Bureau of Reclamation
South Florida Water Management District
City of Plantation

CONTENTS

FIGURES

TABLES

ACKNOWLEDGEMENTS

This project was funded by the WaterReuse Foundation, United States Bureau of Reclamation, South Florida Water Management District, and City of Plantation. Carollo Engineers gratefully acknowledges the WateReuse Foundation's financial, technical, and administrative assistance in funding and managing the project through which this information was discovered. Specifically, the project team is indebted to the following individuals for their cooperation and participation in this project:

Principle Investigator
Jess Brown, Ph.D., P.E., Carollo Engineers, P.C.

Co-Principle Investigator
Jose L. Lopez, P.E., South Florida Water Management District

Project Manager
Andrew T. Salveson, P.E., Carollo Engineers, P.C.

Research Project Team
Don Sullivan, Hank Breitenkam, Zoraida Gonzalez, *City of Plantation*
Dr. Zhi Zhou, Sean Poust, Dr. Keith Bourgeous, Olivia Virgadamo, Dr. Graham Juby, Susanna Li, Dr. Balakrishnan Narayanan, *Carollo Engineers, P.C.*
Richard Cisterna; Enrique Vadiveloo, Tony Greiner, Robert Harris, Robert E. Fergen, Patrick Davis, *Hazen and Sawyer*
Kevin Alexander, *Separation Processes, Inc.*
Debbie Frank, Bradley Cahoon, *Montgomery-Watson Harza*
David Barber, Nancy Denslow, Kevin Kroll, *University of Florida at Gainesville*
Dr. Jocelyn Hemming, *Wisconsin State Laboratory of Hygiene*
Maria Loinaz, Josepth Hughes, Peter deGolian, Mikkel Anderson, Claus Jørgensen, Dorte Rasmussen, and Morten Birkved, *DHI Water and Environment*
Isabel Johnson, *Golder Associates*
Peter Myers, *Hydrosphere Research*

Technical Advisory Committee
Carlyn Kowalsky, *South Florida Water Management District*
Mark Elsner, *South Florida Water Management District*
Jennifer Jurado, *Broward County Environmental Protection Department*
David Lee, *Broward County Environmental Protection Department*
Dr. Jorg Drewes, *Colorado School of Mines*
Dr. Shane Snyder, *Southern Nevada Water Authority*
Dr. Erin Snyder, *Formerly of Intertox*

Project Advisory Committee
Anna Durden, *WaterReuse Foundation*
Dr. Richard C. Pleus, *Intertox*
Anthony Andrade, *Southwest Florida Water Management District*
Lisa Prieto, *Camp, Dresser, & McKee*
Dr. David York, *Florida Department of Environmental Protection*
Ken Yokoyama, *United States Bureau of Reclamation*

EXECUTIVE SUMMARY

Advanced wastewater treatment (AWT) can effectively remove the majority of pollutants. However, the remaining microconstituents (including potential endocrine disrupting compounds, pharmaceuticals and personal care products) in reclaimed water may raise public health and/or aquatic health concerns. Although certain microconstituents may persist following wastewater treatment (Gomez et al., 2007; Stackelberg et al., 2004), current research suggests that advanced treatment technologies can effectively remove them (Tang et al., 2006) to concentrations below human health risk levels (Snyder et al., 2006a). In addition, some research suggests that advanced treatment technologies following conventional wastewater treatment can significantly reduce the risk to aquatic organisms (Schwatter et al., 2007) and that some microconstituents found in municipal wastewater have only negligible effects on invertebrates and plants in the effluents and receiving environment (Brun et al., 2006). However, existing literature also indicates that some microconstituents at or above 0.1 ng/L will induce endocrine-mediated changes in aquatic life (Purdom et al., 1994). Other research suggests that microconstituents, in some cases, have been shown to accumulate in aquatic organisms and alter their natural growth (Kramer et al., 1998; Snyder et al., 2001).

To better understand the removal of microconstituents through AWT facilities and the potential impact of microconstituents to aquatic organisms, an AWT pilot study at the City of Plantation, FL was funded by the WateReuse Foundation (WRF 06-019), the United States Bureau of Reclamation, the South Florida Water Management District (SFWMD), and the City of Plantation, Florida. The AWT facility consisted of a denitrifying filter (DNF), a membrane bioreactor (MBR), ultrafiltration (UF), and reverse osmosis (RO). Benchtop testing was also performed utilizing a non-biological membrane process (IMANS) to examine the role of biological treatment for the removal of microconstituents. In an attempt to correlate microconstituents with biological responses, the toxicological and hormonal impacts to various organisms and cell cultures exposed to effluent from the various AWT processes were evaluated concurrent with chemical analysis.

A secondary objective of this project was to examine the fate and transport of select microconstituents from a hypothetical canal discharge location in South Florida to a drinking water aquifer. To provide presepective on the potential impact to receiving water quality, limited testing of canal water near Plantation , FL was performed.

All three membrane systems (MBR/RO, DNF/UF/RO, IMANS) in this project effectively removed microconstituents and bulk organic matter and salts as measured by BOD_5, TSS, TDS, and tubidity. The results within this report suggest that the discharge of reclaimed RO water may not deteriorate water quality of surface canals, and any of the three tested systems can be used to remove microconstituents and improve the quality of reclaimed water for canal discharge.

The chronic toxicity tests include chronic survival and growth test of *P. promelas* and chronic survival and reproduction test of *C. dubia*. The survivability of *P. promelas* and *C. dubia* in RO effluent were low during the first toxicity test, which was likely caused by chloramine in RO effluent. Additional tests on RO effluent samples that were quenched with sodium thiosulfate significantly reduced toxicity and increased the survivability of *P. promelas* and *C. dubia* in RO effluents. The final batch of toxicity experiments without chloramine indicated that there was no significant difference in RO effluent and control (de-ionized) water for the survival and growth *P. promelas* and survival and reproduction of *C. dubia*. Similarly, there were no significant differences in surface (canal) water and control (de-ionized) water for the survival and growth *P. promelas* and survival and reproduction of *C. dubia*. These fact suggest that discharge of reclaimed water (RO

effluent) has no adverse toxic effect on aquatic organisms. However, unquenched chloramines or trace level of ammonia in AWT facilities may contribute to the toxicity to *C. dubia* and should be removed by break point dechlorination, advanced oxidation, or other quenching methods, and deserves further investigation.

The endocrine disrupting potential of microconstituents in RO effluent were evaluated with E-Screen bioassay, YES assay, fathead minnow Vtg assays and steroid immunoassays. The results of E-Screen bioassay indicate that estradiol equivalents in all RO effluents were below detection limits, even though estradiol equivalents were detected in secondary effluent, DNF effluent, MBR effluents, and UF effluents. The results of E-Screen bioassay indicate that RO effluent did not provoke a significant response in MCF-7 cells. The results of YES bioassay were similar to those of E-Screen bioassays and estradiol equivalents in RO effluents were below detection limits although estradiol equivalents were detected in secondary effluent and DNF effluent, suggesting that RO effluent didn't possess endocrine disrupting potential. The results of fathead minnow Vtg assays and steroid immunoassays did not show an increase of plasma Vtg in male fish, indicating that they are not exposed to estrogenic components at the required concentrations for this effect. The results of steroid immunoassays indicated that testosterone concentrations in all treatments were similar to those in the negative control group and there was no significant difference in plasma testosterone for any of the treatments compared to negative controls. All of these results suggest that RO effluents were not estrogenic.

Three microconstituents (sulfamethoxazole, triclosan, phenol) out of six reviewed representative microconstituents were selected for model development based on their physical/chemical properties. Hydrodynamic and water quality models were developed to examine the fate and transport of these simulated microcroconstituents from the AWT through surface canals. The hydrodynamic model was run for a two-year period (2001 - 2002) and the results indicated that the groundwater results follow the observed data closely, but the surface water results are very sensitive to the structure operations. The water quality model developed predicts that adsorption plays dominant role in the transport of the microconstituents in the canal network as well as in aquifer system. While less significant, various pathways of decay do impact fact and transport of microconstituents. The spreading of microconstituents in the canal network was found to be less for compounds with higher adsorption coefficients. The higher adsorption coefficient decreases the fluctuations in the dissolved concentration in the canals, which is likely a consequence of the adsorbed mass in the sediment layer acting as a buffer. These results confirm that the value of the adsorption coefficient influence how fast the dissolved concentration changes in the canal network. The water quality model is not calibrated and a future effort should be focused on collecting the data necessary to perform calibration. Further efforts can be directed to a better estimation of the related parameters such as mass organic fraction and bulk density in groundwater layers and in sediment layer.

CHAPTER 1
INTRODUCTION

1. INTRODUCTION

1.1. Background

Advanced wastewater treatment (AWT) can effectively remove the majority of pollutants. However, the remaining microconstituents (including potential endocrine disrupting compounds, pharmaceuticals and personal care products) in reclaimed water may raise public health and/or aquatic health concerns. Although certain microconstituents may persist following wastewater treatment (Gomez et al., 2007; Stackelberg et al., 2004), current research suggests that advanced treatment technologies can effectively remove them (Tang et al., 2006) to concentrations below human health risk levels (Snyder et al., 2006a). In addition, some research suggests that advanced treatment technologies following conventional wastewater treatment can significantly reduce the risk to aquatic organisms (Schwatter et al., 2007) and that some microconstituents found in municipal wastewater have only negligible effects on invertebrates and plants in the effluents and receiving environment (Brun et al., 2006). However, existing literature also indicates that some microconstituents at or above 0.1 ng/L will induce endocrine-mediated changes in aquatic life (Purdom et al., 1994). Other research suggests that microconstituents, in some cases, have been shown to accumulate in aquatic organisms and alter their natural growth (Kramer et al., 1998; Snyder et al., 2001).

1.2. Project Objectives

To better understand the removal of microconstituents through AWT facilities and the potential impact of microconstituents to aquatic organisms, an AWT pilot study at the City of Plantation, FL was funded by the WateReuse Foundation (WRF 06-019), the United States Bureau of Reclamation, the South Florida Water Management District (SFWMD), and the City of Plantation, Florida. The AWT facility consisted of a denitrifying filter (DNF), a membrane bioreactor (MBR), ultrafiltration (UF), and reverse osmosis (RO). As part of a related project, the City of Plantation, the SFWMD, and Hazen and Sawyer (H&S) evaluated the pilot treatment trains for the removal of conventional pollutants including suspended solids, total dissolved solids, biochemical oxygen demand, and nutrients. For WRF 06-019, Carollo led the monitoring effort for the removal of microconstituents through the AWT processes, while Plantation and Hazen and Sawyer operated the AWT facilities. In an attempt to correlate microconstituents with biological responses, the toxicological and hormonal impacts to various organisms and cell cultures exposed to effluent from the various AWT processes were evaluated concurrent with chemical analysis. A secondary objective of this project was to examine the fate and transport of select microconstituents from a hypothetical canal discharge location to a drinking water aquifer. The potential discharge of highly treated reclaimed water may be part of an effort to expand wastewater reuse throughout SFWMD's 16-county service area. SFWMD has evaluated the feasibility of using highly treated reclaimed water for augmentation of freshwater flows to several canals and other natural areas in Southeast Florida to offset a portion of the demand for water from the Okeechobee-Everglades Regional Water Management System. To provide presepective on the potential impact to receiving water quality, limited testing of canal water near Plantation , FL was performed.

1.3. Literature Review

What follows is intended as a brief literature review to provide perspective on this project, and is not a comprehensive compilation on the listed topics. The covered topics include the definition, sources, occurrence, health impacts, regulations, and removal of microconstituents.

1.3.1. Microconstituents

1.3.1.1. Definition

Microconstituents are substances that interfere with functioning of the endocrine system in humans or other animals. Microconstituents was defined by the Water Environment Federation (WEF) as "natural and manmade substances, including elements and inorganic and organic chemicals, detected within water and the environment." There are many terms for microconstituents. Alternative terms used to describe these chemicals include: "endocrine disrupting chemicals (EDCs)", "endocrine disruptors", "hormonally active agents", "endocrine active substances", "pharmaceuticals and personal care products (PPCPs)", "pharmaceutically active compounds (PhACs)", "compounds of potential concern (CPC)", "pollutants of concern. (PC)", "emerging contaminants (ECs)", "emerging pollutants (EPs)", "emerging chemicals of concern (ECCs)", "compounds of potential concern", "unregulated contaminants," "persistent bioaccumulative toxins", "trace organic compounds (TOrCs)", "microcontaminants", and similar variations. One of the most common term, though not all encompassing, is the EDC term. Currently, there is no consensus among experts regarding the definition of an EDC or the criteria that should be used to determine whether a chemical is or is not an EDC. Some definitions require that an effect must be demonstrated *in vivo* (i.e., in a live animal), while others stipulate only that the potential for an effect be demonstrated, e.g., through *in vitro* receptor binding or structure-activity relationships (SARs). Other definitions seek to distinguish adverse effects from merely compensatory responses (a non-adverse but measurable effect) (Damstra et al., 2002; EPA-EDSTAC, 1998), but this also has been a source of controversy. The term "microconstituents" is a broad term that does not prejudge the impact of various trace level compounds in water.

Hundreds of chemicals have been implicated as potential microconstituents based on a variety of criteria (IEH, 2005). While screening-level evidence such as SARs, *in vitro* receptor binding activity, and certain short-term *in vivo* tests might suggest the potential for endocrine disruption, such effects often are not demonstrated in the more definitive *in vivo* tests (e.g., tests conducted on multiple generations of exposed animals). Standardized test methods are generally unavailable. At this time, only certain *in vivo* bioassays conducted with intact animals and using appropriate protocols (e.g., encompassing susceptible life stages) provide data that are useful for risk assessment, and few chemicals have been subjected to this type of testing due to the cost and time required to conduct them. Most chemicals have not been tested by any means for endocrine activity.

The United States Environmental Protection Agency (U.S. EPA) established the Endocrine Disruptor Screening Program (EDSP) to develop a battery of standardized toxicity tests that can be used to determine whether a particular chemical is an EDC by U.S. EPA's definition (EPA-EDSP, 2008). The program focuses exclusively on chemicals that act by interfering with estrogen, androgen, or thyroid action (EPA-EDSP, 2008); these are the best characterized modes of action. However, EDCs may also interfere with the functions of other hormones (WHO, 2002). The process will use a two-tiered testing strategy, with Tier 1

consisting of screening-level tests and Tier 2 consisting of *in vivo* bioassays that will generate data suitable for use in risk assessments(EPA-EDSP, 2008). This process is not yet complete, but Tier 1 screening of an initial set of chemicals is expected in 2008 (EPA, 2007).

1.3.1.2. Sources and Occurrence in the Water Cycle

Known or potential microconstituents encompass a wide variety of chemicals and a diversity of structures. They include both natural and synthetic chemicals (Table 1.1). Microconstituents arising from natural sources include hormones excreted by humans and other animals, substances found in plants (phytoestrogens, phytosterols) or fungi (mycoestrogens), metals, inorganic ions, and byproducts of natural combustion processes (e.g., volcanic activity, forest fires) (IEH, 2005; WHO, 2002). Some of these microconstituents occur normally in the environment or in dietary items, but their concentrations may be elevated due to human activities. For example, metals may be mobilized in the environment during mining (Wilkin, 2007), and endocrine-active phytosterols may be released to water in effluents from processing of forest products (MacLatchy et al., 1997; Mellanen et al., 1996). Synthetic microconstituents include certain biocides (pesticides, herbicides, and fungicides) and their degradates, pharmaceuticals and personal care products (PPCPs, including veterinary and human drugs), industrial chemicals and intermediates or byproducts in their production as well as their environmental degradates, and combustion byproducts that are not produced intentionally but result from human activities such as burning of fossil fuels and incineration of industrial and municipal waste (IEH, 2005; WHO, 2002).

Table 1.1.Examples of known or potential microconstituents

	Chemical Class	Representative Chemicals
Naturally-occurring	Hormones	Estradiol, estrone
	Phytoestrogens and plant sterols	Genistein, ß-sitosterol
	Mycoestrogens	Zearalenone
	Metals	Arsenic, cadmium, lead, mercury
	Inorganic ions	Perchlorate, thiocyanate
	Combustion byproducts	Dioxins, certain PAHs
Synthetic	Biocides or their degradates	Atrazine, DDT (or DDE), tributyltin
	PPCPs	Ethynylestradiol, trenbolone
	Industrial chemicals, intermediates, byproducts or degradates	PCBs, bisphenol-A, octylphenol
	Combustion byproducts	Dioxins, certain PAHs

Notes:
PAHs, polycyclic aromatic hydrocarbons; DDT, Dichloro-Diphenyl-Trichloroethane; DDE: p,p'-Dichlorodiphenyldichloroethylene; PCBs, polychlorinated biphenyls

Effluents from municipal wastewater treatment plants (WWTPs) have been implicated as a major source to surface waters (Anderson, 2005). WWTPs receive microconstituents from sources including plant material, plastics, items treated with fire retardants, cleaning products, pesticides, other household chemicals and consumer products, hormones excreted by humans, and PPCPs excreted or washed from the body or flushed to the sanitary sewer. WWTPs might also treat industrial or hospital effluents and stormwater runoff that contain microconstituents from the same and additional sources. Although wastewater treatment processes remove some microconstituents to varying degrees, recalcitrant chemicals may remain at detectable levels in WWTP effluents. If discharged to surface water or groundwater, microconstituents may be diluted, sequestered (e.g., in sediment), or degraded

by physical or biological processes, but some persist in the environment or are detected due to relatively constant loading.

WWTP effluents and reclaimed water are not the only sources of microconstituents to the environment or even to water. Examples of other potential sources include private septic systems (Swartz et al., 2006); untreated storm water flows and urban runoff (Boyd *et al*., 2004); industrial effluents(Boyd et al., 2004); landfill leachate (Coors et al., 2003); discharges from fish hatcheries and dairy facilities (Kolodziej et al., 2004); fish spawning in natural waters (Kolodziej et al., 2004); runoff from agricultural fields and livestock enclosures(Orlando et al., 2004), and land amended with biosolids or animal manure (Hanselman et al., 2003; Khanal et al., 2006).

Various microconstituents have been reported to occur in WWTP effluents, surface water, ground water, reuse water, and drinking water, usually at concentrations in the ng/L (0.000000001 g/L) range. In general, microconstituents are reported to occur with greatest frequency and at highest levels in WWTP effluents. Due to dilution and environmental degradation, concentrations and frequency of detection are typically less for surface water after transportation in the environment (Barel-Cohen et al., 2006; Baronti et al., 2000; Ternes et al., 1999). Based on limited information, microconstituents generally occur only at exceedingly small levels and very infrequently in finished municipal drinking water because they are diluted and undergo degradation in the environment and then must survive advanced drinking water treatment processes to remain in potable water at the tap (Falconer, 2006; Kim et al., 2007; Rodriguez-Mozaz et al., 2004; Westerhoff et al., 2005)

1.3.1.3. Microconstituents Properties

The name, uses, and properties of examined microconstituents for this project are listed in Table 1.2. Their chemical structures are shown in Appendix A.

Table 1.2.Chemical names, uses, and properties of examined microconstituents

Name	Use	Physical Properties[1]		
		Molecular Weight (g/mole)	Solubility (mg/L)	$\log K_{ow}$
2,6-di-tert-butylphenol	UV stabilizer and antioxidant	206.33	2.5	4.92
4-Methyl phenol	dissolvent, disinfectants	108.14	21500	1.94
4-Nonyl phenol	surfactant metabolite	220.36	7	5.76
Acetaminophen	fever relief drug	151.17	14000	0.46
Alpha chlordane	pesticide	409.78	0.056	6.16
Amoxicillin	antibiotic	365.41	3430	0.87
Bisphenol A	anti-inflammatory drug	228.29	120	3.32
Caffeine	stimulant drug	194.19	21600	-0.07
Carbamazepine	anticonvulsant drug	236.28	17.7	2.45
Carbaryl	insecticide	201.23	110	2.36
Chlorpyrifos	insecticide	350.59	1.12	4.96
N,N-diethyl-m-methylbenzamide	insect repellent chemical	191.28	912	2.18
Diazinon	insecticide	304.35	40	3.81
Dieldrin	insecticide	380.91	0.195	5.40
Estradiol	sex hormone	272.39	3.6	4.01
Estrone	estrogenic hormone	270.37	30	3.13

Name	Use	Physical Properties[1]		
		Molecular Weight (g/mole)	Solubility (mg/L)	$\log K_{ow}$
Ethynyl estradiol 17-alpha	oral contraceptive pill	296.41	11.3	3.67
Fluoxetine	antidepressant drug	309.33	60.3	4.05
Gemfibrozil	lipid lowering drug	250.34	10.9	4.77
Ibuprofen	anti-inflammatory drug	206.29	21	3.97
Iopromide	radiopaque contrast agent	791.12	23.8	-2.05
Methyl parathion	pesticide	263.21	37.7	2.86
Phenol	resins, nylons, disinfectant	94.11	82800	1.46
Progesterone	steroid hormone	314.47	8.81	3.87
Sulfamethoxazole	antibiotic	253.28	610	0.89
Tris(1,3-dichloro-2-propyl) phosphate	flame retardant	430.91	7	3.65
Testosterone	steroid hormone	288.43	23.4	3.32
Triclosan	antibiotic	289.55	10	4.76
Trimethoprim	antibiotic	290.32	400	0.91
Triphenyl phosphate	flame retardant and plasticizer	326.29	1.9	4.59
Tris(2-butoxyethyl) phosphate	floor polishes and plasticizer	398.48	1100	3.75
Tris(2-chloroethyl) phosphate	flame retardant	285.49	7000	1.44

Notes:
1. Interactive PhysProp Database (http://www.syrres.com/esc/physdemo.htm)

1.3.1.4. Implications for Aquatic Organisms

Typical biological impact on wildlife of microconstituents may include:

- feminization of male fish or masculinization of female fish;
- delayed sexual development in fish;
- intersex of frogs;
- delayed metamorphosis in frogs;
- embryo mortality;
- abnormal hormone levels;
- impaired reproductive systems and immune systems;
- structual and neurological damage.

There is a substantial and growing body of evidence indicating that microconstituents at levels found in WWTP effluents can cause endocrine disruption in fish and other aquatic life, with the literature suggesting that some microconstituents at or above 0.1 ng/L will induce endocrine-mediated changes in aquatic life (Purdom et al., 1994; Vanderford et al., 2003). This issue first gained public attention when male fish collected downstream of WWTPs in the United Kingdom (U.K.) were found to have elevated levels of vitellogenin, a female-specific egg yolk protein, in their blood. Vitellogenin induction in male fish is a symptom of exposure to estrogens from external sources. Vitellogenin induction generally is not considered to be an adverse effect. Later studies suggest a link between exposure to WWTP effluents and adverse or potentially harmful effects on the reproductive organs and fertility of fish (Jobling et al., 2002; Jobling and Tyler, 2003). The findings in the U.K. studies spurred research in other European countries (Diniz et al., 2005; Petrovic et al., 2002), North America (Bevans et al., 1996; Folmar et al., 2001; Folmar et al., 1996; Giesy et al., 2003; Hemming et al., 2004; Nicholas et al., 1999; Patino et al., 2003; Schoenfuss et al., 2002; Snyder et al., 2004; Woodling et al., 2006), and elsewhere, where WWTP effluents also have been implicated in endocrine-related effects on fish.

WWTP effluents contain a mixture of microconstituents, and in most cases researchers have been unable to pinpoint the specific chemicals responsible for effects indicating endocrine disruption in exposed fish. Estradiol, estrone, ethynylestradiol, nonylphenol, octylphenol, alkylphenol ethoxylates, and bisphenol A have been identified as potential causes (Purdom et al., 1994; WHO, 2002) based on their concentrations in effluents and their potency in laboratory studies. Natural hormones produced in the bodies of humans and other animals (e.g., estradiol and estrone) and synthetic hormones intended to mimic the actions of endogenous hormones (e.g., the oral contraceptive ingredient ethynylestradiol) are particular concerns because they are potent at very small concentrations and are commonly detected in WWTP effluents.

While hormonal disruption of aquatic life by wastewater derived EDCs has clearly been demonstrated, limited information exists on the possibility of long-term aquatic life population effects. This is an area for further research.

1.3.1.5. Impact for Human Health

Although there are well substantiated links between environmental exposure to microconstituents in water supplies (Blazer et al., 2007) and effects in fish, there is little evidence to suggest that typical low-level environmental exposures to microcontituents (in WWTP effluent, reclaimed water, and drinking water) have had any adverse effect on human health (WHO, 2002). Global Water Research Coalition (GWRC) concluded that uptake of microconstituents by humans from treated drinking water is relatively low in comparison to other sources such as foods (GWRC, 2003). There are important differences in exposure to wastewater contaminants between fish and humans. Fish may be immersed in effluents at their point of entry into surface water where concentrations are greatest and can take up contaminants directly across body surfaces, particularly the gills. Fish can also be exposed to microconstituents and other effluent contaminants that accumulate in their food or associate with particulate material and sediments. In contrast, people tend to receive little direct exposure to microconstituents in WWTP effluent, so concerns related to potential human health effects generally center around drinking water contamination. Microconstituents discharged in WWTP effluents or reclaimed water to surface water or groundwater undergo dilution, environmental degradation, and water treatment processes that can substantially reduce their concentrations before they reach the tap. However, the science of endocrine disruption is relatively new, and research into exposure to microconstituents and the potential human health consequences of these exposures continues.

1.3.1.6. Regulations

Although some chemicals that might be considered to be microconstituents are regulated in WWTP effluent for the protection of aquatic organisms, regulations, with one noted exception, are not based on endocrine modes of action except to the extent that they are captured in effects on more traditional ecotoxicologic endpoints (e.g., mortality, reproduction) (EPA, 2005). Likewise, chemicals that might be classified as microconstituents are federally regulated in drinking water, but not on the basis of their potential to cause endocrine disruption. In Massachusetts, the level of perchlorate in drinking water is regulated on the basis of its potential to act as an EDC (i.e., by interfering with thyroid function) (Massachusetts DEP, 2006), but to date no other state has regulated any drinking water contaminant as a putative EDC. The State of California Department of Public Health (CDPH) has mandated monitoring and reporting for a list of potential microconstituents for indirect potable reuse projects in California (CDPH, 2008).

1.3.2. Removal of Microconstituents

This project was primarily an evaluation of membrane systems for removal of microconstituents in wastewater. However, as the results of this study will show, select microconstituents may pass through RO membranes at very low levels. Thus, it is prudent to consider further reduction of microconstituents through biological (as part of secondary treatment) or chemical oxidation processes. This literature review includes information related to these two processes and also includes a brief review of other useful processes, specifically activated carbon adsorption, membrane filtration, and enzymatic treatment.

Several comprehensive studies were conducted to compare the removal efficiency of various processes. One study of full- and pilot-scale drinking water and wastewater treatment processes demonstrated that most conventional drinking water treatment methods were relatively inefficient for contaminant removal, while GAC can effectively remove microconstituents (approximately equal to 99%) in drinking water treatment (Kim et al., 2008). Membrane bioreactors (MBRs) showed limited removal of most microconstituents (wastewater treatment plant study), with the exception of selected hormones and pharmaceuticals (e.g., acetaminophen, ibuprofen, and caffeine). Membrane filtration processes using RO and NF showed excellent removal (>95%) for all targeted microconstituents in wastewater treatment (Kim et al., 2007). For UV process, the use of UV and H_2O_2 or O_3 that can generate OH radicals was capable of degrading the microconstituents faster than UV radiation alone in a batch reactor (Kim et al., 2008). Snyder et al (2007) evaluated the efficacy of various membranes and activated carbons for the removal of microconstituents, and found that granular activated carbon, NF, and RO were more effective at removing a suite of structurally diverse microconstituents than MF and UF. However, the results also showed that the activated carbon filters need regular regeneration and non-regenerated activated carbon filters displayed no removal of microconstituents (Snyder et al., 2007). Drewes et al. found that that lower pressure, high intensity UV radiation did not remove microconstituents, medium range UV radiation and chlorination only partially removed phenolic compounds, while activated carbon, high-pressure membranes, and soil-aquifer treatment can effectively remove microconstituents and reduce biological activity to below detection in reclaimed water (Drewes et al., 2006a).

1.3.2.1. Conventional Activated Sludge

Most microconstituents could not be effectively removed by conventional activated sludge. A study at a municipal wastewater treatment showed that only 4 out of 35 microconstituents were degraded by more than 90% while 17 compounds are removed by less than 50% (Joss et al., 2006). In another study in Japan, 66 microconstituents could not be efficiently removed using physico-chemical wastewater treatment after conventional activated sludge treatment (Okuda et al., 2008). The removal efficiencies of carbamazepine and crotamiton were less than 30%. Conversely, ozonation process followed by biological activated carbon process could efficiently reduce all the residual microconsituents below their quantification limits (Okuda et al., 2008).

Similarly, the average removal efficiency of tested microconstituents in 12 sewage treatment plants in Finland was less than 65% and the removal efficiency varied greatly between the treatment plants. Fluoroquinolones were eliminated by more than 80% in the treatment plants, while carbamazepine was removed poorly and even increased in the treated sewages, possibly due to enzymatic cleavage of the glucuronic conjugates of carbamazepine (Vieno et al., 2007a).

In another study, the removal efficiency of acidic microconstituents (ibuprofen, naproxen, mefenamic acid, ketoprofen, and diclofenac), caffeine, and triclosan during secondary treatment ranged from 51 to 99% (Thomas and Foster, 2005).

1.3.2.2. Coagulation

The removal of selected microconstituents (diclofenac, ibuprofen, bezafibrate, carbamazepine and sulfamethoxazole) by chemical coagulation was studied in jar tests (Vieno et al., 2006). In Milli Q water coagulation, the microconstituents were poorly removed (< 10%) with the exception of diclofenac (66% with ferric sulphate). In lake water cogulation, only diclofenac was removed (30%) with ferric sulphate. In the presence of dissolved humic matter, diclofenac as well as ibuprofen and bezafibrate could be removed by ferric sulphate coagulation. Although conditions such as high humic material content, low coagulation pH and ferric coagulant can increase the removal of certain ionic microconstituents, it was determined that coagulation can not effectively remove microconstituents from water (Vieno et al., 2006). The removal of 18 microconstituents (and metabolites) and 7 s-triazines herbicides were evaluated and the flocculation-coagulation and dual media filtration steps without ozone treatment resulted in no decrease in analyte concentrations, while ozonation removed 66-100% (< 0.05-1 ng/L) of the microconstituents and is highly effective in depleting carbamazepine, caffeine, cotinine, and atrazine in drinking water treatment processes (Hua et al., 2006). Similarly, the removal efficiency of 13 studied microconstituents was only 13% following coagulation, sedimentation, and rapid sand filtration, but the following ozonation at 1 mg/L removed all microconstituents below detection limits except ciprofloxacin in a pilot-scale drinking water treatment plant (Vieno et al., 2007b). The removal of some selected microconstituents in sewage (galaxolide, tonalide, diazepam, carbamazepine, ibuprofen, naproxen, diclofenac) by coagulation-flocculation were around 50-70%, except that carbamazepine and ibuprofen were not removed at all. Conversely, flotation removed galaxolide and tonalide by 35-60%, followed by diazepam (40-50%), diclofenac (20-45%), carbamazepine (20-35%), ibuprofen (10-25%), and naproxen (10-30%) (Carballa et al., 2005). It is apparent that coagulation is more effective in waters with high organic content, possibly related with the cogulation removal of particles with sorbed microconstituents.

1.3.2.3. Activated Carbon Adsorption

Activated carbon has been found to be effective to remove microconstituents. In the same study by Vieno et al, granular activated carbon adsorption (GAC) effectively removed 10 microconstituents except for three hydrophilic microconstituents (atenolol, sotalol, and ciprofloxacin) in a pilot-scale drinking water treatment plant (Vieno et al., 2007b).

Activated carbon adsorption can also effectively remove estrone and 17 β-estradiol in pure water, however the absorbability of estrone and 17 β-estradiol in river water and secondary effluent reduced significantly, possibly due to site competition and pore blockage and the presence of surfactant and humic acid (Fukuhara et al., 2006; Zhang and Zhou, 2005). In another study at a conventional drinking water treatment plant, GAC adsorption accounted for 53% of the removal of 113 organic compounds including microconstituents, while chlorination and clarification accounted for 32% and 15% of the removal of 113 organic compounds (Stackelberg et al., 2007).

The removal of microconstituents in secondary effluent by coagulant-assisted GAC was investigated and the results showed that coagulant-assisted GAC adsorption removed most

microconstituents except carbamazepine, clofibric acid, gemfibrozil, ibuprofen, p-toluenesulfonamide, caffeine, butylated hydroxyanisole, butylated hydroxytoluene, and N-butyl benzenesulfonamide (Soliman et al., 2007).

1.3.2.4. Membrane Bioreactor

A nembrane bioreactor (MBR) was found to perform better than a conventional activated sludge system in removing microconstituents and in the removal of estrogenicity. Radjenociv et al found the performance of MBR to be better (removal rates >80%) than a conventional activated sludge system for most of the investigated microconstituents. Carbamazepine was the most persistent pharmaceutical and it passed through both the MBR and activated sludge systems untransformed (Radjenovic et al., 2007). Oestrogen and 17beta-oestradiol can be effectively removed (Chang et al., 2006). However, substantial amounts of estrone, estrone-3-sulfate, estrone-3-glucuronide, and 17 beta-estradiol-glucuronides passed through treatment systems (Hu et al., 2007a). Bisphenol A (BPA) was removed well with a removal efficiency of 68.9 -90.1%, but 4-nonylphenol concentration was amplified after MBR treatment which could be caused by the transformation of its parent compounds, nonylphenol polyethoxylates (Hu et al., 2007a). The removal of 19 microconstituents by a MBR was evaluated and more than 90% of bisphenol-A, ibuprofen, or bezafibrate were removed, while no carbamazepine was removed (Clara et al., 2005).

The removal efficiency by MBRs is related to sludge retention time (SRT) as activated sludge treatment but can reach a higher SRT with a compact MBR reactor than conventional activated sludge treatment system (Clara et al., 2005). The effect of SRT on microconstituent removal was confirmed in another study (Kimura et al., 2007). The removal of six acidic microconstituents (clofibric acid, diclofenac, ibuprofen, ketoprofen, mefenamic acid, and naproxen) in a wastewater treatment plant (WWTP) using an activated sludge system and MBRs were evaluated and the SRTs of the WWTP and the two MBRs were 7, 15, and 65 days, respectively. The MBRs exhibited greater removal rates for the examined six acidic microconstituents then the WWTP, possibly due to the longer SRTs. The MBR operated with a longer SRT of 65 days also showed better performance than did the MBR with a shorter SRT of 15 days. Batch elimination tests revealed that the main mechanism of elimination of the microconstituents was due to biodegradation (Kimura et al., 2007).

1.3.2.5. O_3/H_2O_2/UV Oxidation

Advanced oxidation of wastewater using ozone (O_3), O_3/UV or H_2O_2/UV successfully led to the reduction of carbamazepine, diazepam, diclofenac, and clofibric acid to below detection, although these microconstituents were poorly removed by biological treatment in conventional activated sludge and in MBRs (Gebhardt and Schroder, 2007).

Ozone and Ozone/H_2O_2 oxidation are effective techniques to reduce microconstituents. In a wastewater study (filtered secondary effluent), the majority of target microconstituents were reduced by greater than 90% by O_3, while atrazine, iopromide, meprobamate, and tris-chloroethylphosphate were removed less than 50%. The addition of H_2O_2 for advanced oxidation was of little benefit for contaminant removal as compared to O_3 alone. O_3/H_2O_2 provided a marginal increase in the removal of dilantin, diazepam, DEET, iopromide, and meprobamate, while decreasing the removal efficacy of pentoxifylline, caffeine, testosterone, progesterone, and androstenedione (Snyder et al., 2006b).

The removal efficiency of six microconstituents (4-n-nonylphenol, bisphenol A, 17 α -ethinylestradiol, 17 β -estradiol, estrone, and estriol) by ozonation was over 95% with ozone exposures of 2 x 10^{-3} mg*min/L in water treatment processes (Deborde et al., 2005), confirming that ozonation can effectively remove 17 α-ethinylestradiol, estrone, and estradiol (Huber et al., 2004). The estrogenicity was reduced by a factor of more than 200 after ozonation using YES assays (Huber et al., 2004). Similarly, macrolide and sulfonamide antibiotics, estrogens, and the acidic microconstituents diclofenac, naproxen, and indomethacin were oxidized by more than 90-99% for O_3 doses over 2 mg/L in a pilot-scale column study of municipal wastewaterwith suspended solids have only a minor influence on the oxidation efficiency of nonsorbing micropollutants (Huber et al., 2005a). During ozonation of a natural estrogen (17 β-estradiol) in water, several by-products were formed at pH 7 and 11, while only testosterone could be observed in pH 3. Higher estrogenic activity was detected at pH 11 using YES assay, possibly because the oxidation via OH radical forms more by-products with estrogenic activity. Complete removal of estrogenic activity was only obtained at pH 3 (Bila et al., 2007). The removal of 17 β -estradiol and bisphenol A by O_3 only and O_3/UV advanced oxidation were compared and the results showed that coupling of UV decreased the O_3 consumption by 22.5% in converting the same amount of 17 β -estradiol, while there was no significant difference in O_3 consumption for complete conversion of BPA by O_3 and O_3/UV systems (Irmak et al., 2005).

The removal efficiency of BPA with an initial concentration of 1.0 mg/L was measured up to 70%, 82%, 90% within 30 minutes when the dosage of ozone was 1 mg/L, 1.5 mg/L, 2 mg/L respectively, and the results showed that major degradation of BPA was contributed by ozone dosage instead of contact time (Xu et al., 2006). Another study indicated complete removal of BPA in water by ozonation, and the direct reaction rate constants were 1.3 x 10^4 $M^{-1}s^{-1}$ for BPA at pH = 2 and 1.6 x 10^9 $M^{-1}s^{-1}$ for dissociated BPA at pH = 12. Use of hydrogen peroxide did not alter the main degradation route and the molecular ozone remained a principal oxidant as a substantial portion of the OH radical is scavenged by hydrogen peroxide. (Lee et al., 2003). Another study on the degradation and mineralization of BPA in water by UV/H_2O_2/micro-aeration process showed that the mineralization rate of BPA increases linearly with the enhancement of intensity of UV radiation. When the dosages of H_2O_2 change from 5 mg/L to 20 mg/L, the mineralization rate of BPA raised 8-fold (Hu et al., 2007b).

Ozonation can also remove more than 80% of the phenolic antiseptics, crotamiton, sulfonamide and macrolide antibiotics, and 17β-estradiol among 24 microconstituents during sand filtration and ozonation, while sand filtration was generally inefficient to remove microconstituents, probably because of their low hydrophobicities. The combination of ozonation and sand filtration with activated sludge treatment gave efficient removal (>80%) of all the target compounds except carbamazepine and diethyltoluamide (Nakada et al., 2007).

N-nitrosodimethylamine (NDMA), a carcinogenic microconstituent, can be effectively removed by O_3/H_2O_2 oxidation, even though it can't be effectively removed by membrane filtration. The results indicated that the reaction with hydroxyl radical dominates the NDMA oxidation during ozonation. Conventional ozonation with up to 160 mM ozone led to less than 25% NDMA oxidation in natural waters, and the O_3/H_2O_2 oxidation with 160-320 mM ozone can achieve 50-75% NDMA oxidation. However, multiple injections of ozone can improve the oxidant utilization efficiency. Bromate formation may be the limiting factor for NDMA oxidation during ozonation and O_3/H_2O_2 oxidation in bromide-containing waters (Lee et al., 2007).

The removal efficiency of microconstituents in drinking water by ozonation can be affected by the water compositions, with the highest removal efficiency found in ultrapurified water, while other factors such as filtered water and river water reduced the removal efficiency by 26.5% - 50.3% and 57.3% - 72.0%, respectively (Liu et al., 2007). A 3D quantitative structure-property relationship (QSPR) model was developed as to evaluate removal mechanisms during chlorination and ozonation in typical water treatment processes (Lei and Snyder, 2007).

UV was shown to be effective to remove select microconstituents. It was found that more than 90% of di-n-butyl phthalate (DBP) can be degraded within an hour of UV irradiation at 254 nm, especially in neutral to basic conditions. The major decomposition mechanism of DBP is believed to involve the hydrolytic photolysis of the carbon in the alpha and/or beta-position of the ester chain with the production of aromatic carboxylic derivatives (Lau et al., 2005).

Bisphenol A, ethinyl estradiol, and estradiol were more effectively degraded utilizing UV/H_2O_2 advanced oxidation as compared to direct UV photolysis treatment (Rosenfeldt and Linden, 2004). The UV/H_2O_2 processes using either low or medium pressure lamps can degrade microconstituents in lab water by 80 and 99.3% at a 15 ppm H_2O_2 concentration and a UV dose of 1,000 mJ/cm^2. The results indicated that a dose of less than 200 mJ/cm^2 completely removed oestrogenic activity in lab water (Linden et al., 2007).

The kinetics of Ultraviolet C (UV-C)-induced direct phototransformation of four microconstituents (17 α-ethinylestradiol, diclofenac, sulfamethoxazole, and iopromide) was investigated in dilute solutions of pure water buffered at various pH values using a low-pressure and a medium-pressure mercury arc lamp. At the UV-C (254 nm) drinking water disinfection dose of 400 J/m^2, the degree of depletion of the select microconstituents at pH=7.0 in pure water was 0.4% for 17-alpha ethynyl estradiol, 27% for diclofenac, 15% for sulfamethoxazole, and 15% for iopromide, indicating that phototransformation should be seriously taken into account when evaluating the possibility of formation of UV transformation products (Canonica et al., 2008).

1.3.2.6. Chlorination

The removal efficiency of ClO_2 oxidation was only effective to oxidize certain microconstituents such as the investigated sulfonamide, macrolide antibiotics, and estrogens in lake water and groundwater (Huber et al., 2005b). Similarly to ozonation, chlorination removed 75%-99% of the test microconstituents (BPA, 17 β -estradiol, and 17 α -ethynyl estradiol) in distilled water, however chlorination reached a stabilized estrogenic level in more than 120 min after transformation of test microconstituents while ozone oxidation reached a stabilized estrogenic level in 10 min (Alum et al., 2004).

1.3.2.7. Membrane Filtration

Membrane filtration, such as MF, NF and RO, have been proven effective for the removal of microconstituents.

Canonica et al, found that lime/RO treatment of in secondary effluent at a wastewater treatment plant and two water reclamation facilities removed clofibric acid, ibuprofen, caffeine, butylated hydroxyanisole, and N-butyl benzenesulfonamide from influent levels up

to 71 ng/L to below 10 ng/L, and the MF/RO treatment reduced concentrations to levels below their detection limits except for butylated hydroxytoluene at one facility (Soliman et al., 2007). The removal of pentachlorophenol by low pressure RO membrane was higher than 80%. The rejection increased with the increase of pH (Razak et al., 2007).

The mechanisms of removing microconstituents by NF and RO membranes were shown to be size exclusion and adsorption. Furthermore, deprotonation of estrone led to a significant decrease in retention by a NF membrane, but not for a tight RO membrane, suggesting that the extent of hormone retention may be very susceptible to maintenance of membrane adsorptive capacity and solution chemistry (Schafer et al., 2003). Another study indicated that adsorption (or partitioning) of hormones to the membrane polymer is the dominant removal mechanism at the early stages of NF filtration of hormones, but size or charge exclusion of the membrane dominated at the later filtration stage (Nghiem et al., 2004).

The rejection of microconstituents by a variety of commercial RO, NF, and ultra-low-pressure RO membranes was investigated and the results indicated that the presence of effluent organic matter improved the rejection of ionic organics by tight NF and RO membranes. Rejection of ionic pharmaceutical residues and pesticides ranged from 89% to over 95% by NF membranes. Rejection of hydrophobic nonionic compounds was initially high, but decreased significantly after 10 hours of operation because of solute partitioning through the membranes (Xu et al., 2005). Drewes et al. also evaluated the rejection of microconstituents by high-pressure membranes and identified the following solute parameters affecting microconstituent rejection: molecular weight, molecular size, acid disassociation constant, hydrophobicity/hydrophilicity, and the diffusion coefficient. Membrane properties, such as molecular weight cutoff, pore size, surface charge, hydrophobicity/hydrophilicity, and surface morphology also affect microconstituent rejection. Feed water composition such as pH, ionic strength, hardness, and the presence of organic matter, plays a role on microconstituent rejection as well (Drewes et al., 2006b). In addition, Drewes et al. developed a rejection diagram based on the physicochemical characteristics (dissociation potential, hydrophobicity, molecular size) to predict the rejection of microconstituents. Rejections of the sodium dibasic arsenate, the arsenate anion, and pesticides by the NF membranes are high. The charge exclusion, size exclusion, and the specific physicochemical phenomena were found to be important for the rejections by the NF membranes (Košutić et al., 2005).

The removal of estrone and 17β-estradiol by direct contact membrane distillation (DCMD) and forward osmosis (FO) were investigated for wastewater treatment in advanced life support systems (e.g., space missions), and DCMD provided greater than 99.5% hormone rejection, constant flux, greater than 99.9% urea and ammonia rejection, and high water recovery. Similarly, FO provided from 77 to 99% hormone rejection (Cartinella et al., 2006)

1.3.2.8. Enzymatic Treatment

Enzymatic treatment was found to be efficient to remove microconstituents. A horseradish peroxidase enzyme-catalyzed process was capable of achieving 92-100% removal of estrone, 17 β-estradiol, estriol, and 17 α-ethinylestradiol within 1h of treatment of water with a horseradish peroxidase activity of 0.017μ/mL (Auriol et al., 2006). The effects of temperature, pH, and wastewater constituents significantly impact the horseradish peroxidase-catalyzed estrogen removal (Auriol et al., 2006). In another study, estrone, 17beta-estradiol, estriol, and 17alpha-ethinylestradiol can be completely oxidized in the synthetic water and municipal wastewater after a 1-h treatment with either horseradish

peroxidase (8-10 μ/mL) or laccase (20μ/mL), and both enzymatic treatments were found to be efficient in removing the estrogenic activity of the studied steroid estrogens (Auriol et al., 2008). Estrone can be removed by 98% after 5 d of treatment and the activities of ligninolytic enzymes, possibly due to ligninolytic enzymes produced extracellularly by white rot fungus *Phanerochaete sordida YK-624.* Further experiments showed that estrone was completely removed after 1 h of treatment with either manganese peroxidase or laccase, and both enzymatic treatments completely removed the estrogenic activity of estrone after 2 h, suggesting ligninolytic enzymes are effective in removing estrogenic activity of estrone (Tamagawa et al., 2006).

1.3.2.9. Ferrate(VI) Oxidation

Ferrate (Fe (VI)) can effectively reduce microconstituents to very low levels (10 - 100 ng/L) and ferrate was shown to be more effective than electrochemical oxidation to reduce COD concentration in wastewater (Jiang et al., 2005). The ferrate oxidation of the four steroid estrogens (17 α-ethynylestradiol, estrone, β-estradiol, and estriol) had higher reaction rates than BPA. It is concluded that ferrate oxidation could be an effective treatment method for the purification of waters containing these particular microconstituents (Li et al., 2008). Approximately 90% of the BPA was degraded by ferrate after 60s (Li et al., 2005). The photocatalytic oxidation efficiency in the presence of Fe (VI) was much greater than that without Fe (VI) (Li and Li, 2007), and the effectiveness of Fe (VI) for the oxidative removal of phenolic microconstituents was also confirmed in both natural water and wastewater (Lee et al., 2005). Potassium ferrate (VI) (K_2FeO_4) can be used to remove sulfamethoxazole (Sharma et al., 2006). The extent of degradation of three chlorinated microconstituents (4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol) by Fe (VI) was found to be highly pH dependent (Graham et al., 2004)

In another recent study by Lee et al, the potential of Fe (VI) was assessed to oxidize various microconstituents and remove phosphate by a subsequent ferric phosphate precipitation during treatment of municipal wastewaters. The results showed that Fe (VI) doses less than 8 mg/L are capable of oxidizing many kinds of microconstituents and removing phosphate below 0.8 mg/L. Fe (VI) and O_3 exhibited similar removal efficiencies. Fe (VI) was more stable (minutes) than ozone (seconds) in the tested wastewater due to a slower consumption of ferrate by matrix components. Ozone achieved better removal than Fe (VI) for some microconstituents without reactive moieties (e.g. ibuprofen), due to the formation of OH radicals. (Lee et al., 2008).

1.3.3. Representative Microconstituents for Recharge Modeling

1.3.3.1. Introduction

The recharge modeling of reclaimed water to surface canals was conducted by DHI Water and Environment (DHI). To select the respresentative microconstituents for recharge modeling, DHI completed a limited literature review on the fate and transport of six microconstituents in surface water and in groundwater. This review focused on six of the 32 monitored microconstituents. The six researched microconstituents were chosen based on degradation processes resulting from photolysis, biodegradation, and sorption to organic matter. The selected microconstituents represent a range of different physical/chemical properties, fate processes, and anticipated uses of end products:

- sulfamethoxazole (antibiotic)
- triclosan (antibacterial agent which is widely used in personal care products)

- ibuprofen (non-steroidal anti-inflammatory drug)
- 4 nonyl-phenol (pesticide products)
- methylparathion (insecticide)
- phenol (mainly production of plastic)

The literature review reported decay rates for these microconstituents for each process (photolysis, biodegradation and hydrolysis). Also, Henry constants (necessary to determine evaporation losses) and adsorption coefficients were reported. As discussed further on, three of these six compounds were then selected for modeling of fate and transport as part of this project and compared to a comservative "tracer" compound.

The relevant transport and fate processes for the each of these microconstituents were investigated in both surface water and groundwater. The fate processes were sorption and degradation. Three different degradation processes can be relevant, namely: hydrolysis, photolysis and biodegradation. Typical transport mechanisms are: advection, volatilization of dissolved fraction from the water column to the atmosphere, molecular diffusion into the sediment and turbulent dispersion and sedimentation of sorbed pesticides from water column to the sediment.

The physical-chemical properties of the microconstituents are important in determining the fate of a microconstituents. Among these properties are the octanol-water partition coefficient (Kow), the soil and sediment sorption coefficients (Koc), the water solubility the vapour pressure, the Henry's constant, and the acid-base ionization constant.

The focus of the literature review is to identify the most important removal processes, estimate a simple first-order half-life coefficient to be utilized in the modeling process, and find typical concentrations in surface and ground water after a hypothetical injection of higly treated reclaimed water to a surface water canal.

Estimates of removal half-life for each of the six selected microconstituents and typical removal were obtained by applying the estimation software EPIwin v3.12 from the US. EPA. The software also contains a large database of literature values. If database records were found these were compiled instead of using the estimates.

1.3.3.2. Fate and Transport Parameters

1.3.3.2.1. Sulfamethoxazole

Sulfamethoxazole is an antibacterial sulfonamide. It prevents the formation of dihydrofolic acid, a compound that bacteria must be able to make in order to survive. Although it was once a very useful antibiotic, it is almost obsolete as a single agent today due to the development of bacterial resistance to its effects. Sulfamethoxazole is now used primarily in combination with trimethoprim, a combination product known as Bactrim or Septra. It is commonly used to treat urinary tract infections.

Many the microconstituents are not removed efficiently by coagulation and flocculation processes in wastewater treatment facilities due to relative low Log Kow values. Sulfamethoxazole have a Log Kow of 0.89, the lowest among the selected microconstituents.

Sulfamethoxazole is reported as biodegradable under aerobic conditions in an adapted activated sludge culture. The lag period before initiation of degradation was 4 days (Drillia

et al., 2005). In laboratory studies no significant biodegradation was found in pond water over a period of 30 days (Lam et al., 2004). Kjølholt et al. report that sulfamethoxazole is not biodegradable (Kjølholt et al., 2003).

Ternes et al. reported that 4 of 54 studied pharmaceuticals and personal care products were found below a treated sewage infiltration site (45 years of operation) (Ternes et al., 2007). Three meters below the ground water table (unsaturated zone 1.5 - 2 m) sulfamethoxazole concentrations were between 0% and 20% of input concentrations.

Sulfamethoxazole adsorps UV light and is susceptible to photo-degradation. Half lives in synthetic field water and synthetic sunlight was found to be between 2.7 and 6.6 hours depending on the DOM content (Lam and Mabury, 2005). Mean half-life in 12 microcosms with fish, aquatic plants, zooplankton, phytoplankton, macrophytes, and bacteria was 19 days (Lam et al., 2004).

The typical surface water concentrations of sulfamethoxazole is summarized in Table 1.3.

Table 1.3. Typical reported surface water concentrations of sulfamethoxazole

Type	Location	Minimum (µg/L)	Maximum (µg/L)	Mean (µg/L)	Source
Surface water	Minnesota	0.0039	0.5		(Lee et al., 2004)
Surface water	Huron River	0.0037	0.018	0.010	(Skadsen et al., 2004)
Raw Waste water	Ann Arbor	0.23	1.2	0.69	(Skadsen et al., 2004)
WWTP effluent	Ann Arbor	0.35	0.86	0.56	(Skadsen et al., 2004)
Surface water	Boulder creek	0.052	0.220		(Barber et al., 2000)

1.3.3.2.2. Triclosan

Triclosan is used as a preservative and an antibacterial agent that is widely found in personal care products such as shampoos, soaps, cosmetics, lotions, toothpaste as well as cleaning materials, paint, textiles, and plastic products.

Studies regarding the fate and effects of triclosan have been reviewed by Samsøe-Petersen et al. to describe the fate of triclosan in wastewater treatment plants (WWTPs) and to make environmental risk assessments of Triclosan (Samsøe-Petersen et al., 2003). The reviewed studies showed that triclosan degrades under aerobic conditions in WWTPs and is extensively degraded and removed in activated-sludge systems. Furthermore, triclosan does not adversely impact the treatment processes at levels up to 2 mg/L in the influent. However, monitoring studies indicate that little to no removal of triclosan occurs during anaerobic sludge digestion. Monitoring of triclosan concentrations at WWTPs in the U.S.A., Sweden, Switzerland and Denmark showed the following ranges of triclosan concentrations:

- Influent: 0.1-16.6 µg/L
- Effluent: 0.10-2.70 µg/L
- Sludge: 0.028-15.6 µg/g (dry weight)

Studies regarding photolysis of triclosan in surface water have demonstrated that this may be a significant pathway in the upper layers of lakes (e.g. at pH 8, 4.6% of the parent compound was transformed to the dioxin 2,8-DCDD). Such a transformation can, however, only be expected in the upper layers of lakes due to sorption of light in the water column (Samsøe-

Petersen et al., 2003).

A direct photolysis rate of 0.07/day was measured using a water sample from the Greifensee, Switzerland tested under laboratory conditions, corresponding to a photolysis half life in water of 10 days; the elimination rate sum of different transport and transformation processes in this lake is 0.03/day, corresponding to a half life of 21 days (HSDB, 2008).

The triclosan dissipation downstream was estimated using standard first-order kinetics. A first-order rate constant, k, of 0.054 per hour was used. Morral et al. estimate the constant based on a river die away study and corrected for dilution (Morrall et al., 2004). This study is, however, still unpublished and has not been available for the present evaluation. The physico-chemical properties were collected by Reiss et al. and summarized in Table 1.4 (Reiss et al., 2002).

Table 1.4.Physical chemical properties of triclosan

Property	Value
Dissociation constant (pKa)	8.14 at 20 °C
Vapor pressure	$7*10^{-4}$ Pa at 25 °C
Partition coefficient (logKow)	4.8
Aerobic biodegradation in soil	17.4 - 35.2 day half-life
Aqueous photolysis	41 min. half-life at pH 7 and 25 °C
Adsorption to suspended solids (Koc)	47454 mL/g

The following aspects were either not considered significant for the estimation of the exposure concentrations or data were not available (Reiss et al., 2002):

- Aquatic biodegradation or anaerobic degradation - no available studies
- Sorption to biota -no available data
- Biodegradation in benthic sediments - considered negligible
- Aquatic photolysis -considered negligible in the water bodies (inconsistent with table 3, which says 41 minute half-life for aqueous photolysis)

A study designed to determine the die-away rate of triclosan released into a river as part of the sewage treatment plant effluent matrix determined a first-order loss rate from measured data of 0.06 h^{-1}. Mathematical modeling indicated that sorption and settling accounted for approximately 19% of total triclosan loss over 8 km. When removing sorption and settling, the remaining amount of triclosan had an estimated first-order loss rate of 0.25 h^{-1}, which was attributed to a combination of biodegradation and photolysis (Morrall et al., 2004).

Soil batch studies showed that triclosan could be biodegraded with half lives of approximately 18 days under aerobic conditions whereas no degradation was observed under anaerobic conditions (Ying et al., 2007).

According to HSDB a study showed a photolysis half-life in water of 10 days. The typical surface water concentrations of triclosan is summarized in Table 1.5.

Table 1.5.Typical reported surface water concentrations of triclosan

Type	Location	Minimum (µg/L)	Maximum (µg/L)	Mean (µg/L)	Source

Type	Location	Minimum (µg/L)	Maximum (µg/L)	Mean (µg/L)	Source
Surface water	Various	0.0039	0.5	0.30	(Barnes et al., 2002)
Surface water	Huron River	0.088	4.3		(Lee et al., 2004)
WWTP effluent	US	0.24	2.7		(Samsøe-Petersen et al., 2003)
WWTP effluent	Worldwide	2.7			(Samsøe-Petersen et al., 2003)

1.3.3.2.3. Ibuprofen

Ibuprofen is a non-steroidal anti-inflammatory drug. It is used for relief of symptoms of arthritis, primary dysmenorrhoea, fever, and as an analgesic, especially where there is an inflammatory component.

Ibuprofen are generally resistant to hydrolysis. Therefore, hydrolysis is not expected to be an important removal process of ibuprofen from water systems (HSDB, 2008). Ibuprofen is not expected to directly photolyze due to the lack of adsorption in the environmental UV spectrum (>290 nm) (HSDB, 2008).

A OECD Guideline 301B "Ready Biodegradability" Modified sturm test (CO_2 evolution) showed a CO2-evolution between 10% and 60%. Hence the compound is not considered readily degradable (ESIS). It is however degradable to some extent. A half-life of 20 days was determined from a study using water samples from lake Greifensee, Switzerland that were incubated at room temperature for 37 days with 200 ng/L racemic ibuprofen (HSDB, 2008).

A field investigation showed that 4 of 54 studied pharmaceuticals and personal care products were found below a treated sewage infiltration site (45 years of operation). Three meters below the ground water table (unsaturated zone 1.5 - 2 m) ibuprofen was undetectable (Ternes et al., 2007).

The typical surface water concentrations of ibuprofen is summarized in Table 1.6.

Table 1.6.Typical surface and groundwater concentration of ibuprofen

Type	Location	Minimum (µg/L)	Maximum (µg/L)	Mean (µg/L)	Source
Surface water	Huron River		0.0071	0.0025	(Skadsen et al., 2004)
Raw wastewater	Ann Arbor	6.6	23	11	(Skadsen et al., 2004)
Treated wastewater	Ann Arbor	0.011	0.051	0.030	(Skadsen et al., 2004)
Surface water	Various	0.12	0.71		(Lee et al., 2004)
Surface water	Boulder creek			0.108	(Barber et al., 2000)
Ground water	Various			negligible	(Ternes et al., 2007)

1.3.3.2.4. 4 nonylphenol

Nonylphenol and the related nonylphenol ethoxylates are used in pesticide products as "inert" ingredients.

Biodegradation of p-nonylphenol will occur rapidly in aerobic soils, but is inhibited in anaerobic soil conditions. Degradation of 4-n-nonylphenol has been investigated in the laboratory using sediment and groundwater from an aquifer in Bolivar, South Australia. 4-n-

nonylphenol degraded quickly under aerobic conditions with a half-life of 7 days (Ying et al., 2003). Studies of degradation in groundwater have not been identified.

Nonylphenol is susceptible to indirect photolysis. Half-lives of 10-15 hours in both tap water and creek water, under continuous clear skies, at noon, and under summer sunlight conditions, were found at the surface. At a depth of 20-25 cm half-lives were 1.5 times longer (Ahel et al., 1994).

Nonylphenol and its ethoxylates are frequently found in water, though it is difficult to identify contamination resulting from just pesticide-related uses. In a sample of New Jersey drinking water, seven nonyl phenol ethoxylates were found with a total concentration of 725 parts per trillion (ppt). In addition, over 225 ppt nonylphenol carboxylates and over 175 ppt of octylphenol ethoxylates and 49 ppt carboxylates were found. In a US nationwide sampling of rivers with industrial or sewer effluent, 30 percent contained nonylphenol, 33 percent contained nonyl phenol monoethoxylate, 42 percent contained nonylphenol diethoxylate, and 24 percent contained ethoxylates with more ethylene oxide units. The highest concentrations measured were about one part per billion (ppb) for the first three compounds and 15 ppb for the fourth.

Limited information on surface water concentrations of 4 nonylphenol is summarized in Table 1.7.

Table 1.7.Typical surface and groundwater concentration of 4 nonyl Phenol

Type	Location	Minimum (µg/L)	Maximum (µg/L)	Mean (µg/L)	Source
Surface water	Boulder Creek	0.011	0.28		(Barber et al., 2000)

1.3.3.2.5. Methyl parathion

Methyl parathion is an organophosphate insecticide used to control insect pests of agricultural crops, primarily on cotton. It kills insects by contact, stomach and respiratory action. Methyl parathion is available in dust, emulsifiable concentrate, ULV liquid, and wettable powder formulations. Methyl parathion is a highly toxic insecticide in EPA toxicity class I.

In surface waters, methyl parathion degrades by biotransformation, hydrolysis, volatilization, and photolysis (ATSDR, 2008). Methyl parathion degrades rapidly in seawater, lake, and river waters, with 100% degradation occurring within 2 weeks to 1 month or more. Degradation is faster in the presence of sediments, and is faster in fresh water than in salt water. Complete breakdown occurs at a rate of 5 to 11% in 4 days in rivers, and more slowly in marine waters. In water, methyl parathion is subject to photolysis, with a half-life of 8 days during the summer and 38 days in winter (ATSDR, 2008). Biodegradation is expected to be the predominant degradation process. Adsorption to sediment and suspended matter may significantly affect the degradation (ATSDR, 2008).

The degradation of methyl parathion by hydrolysis and biodegradation was studied in four types of water (ultrapure water, pH 6.1; river water, pH 7.3; filtered river water, pH 7.3; and seawater, pH 8.1) maintained at 6 and 22 °C, in the dark. The half-lives of methyl parathion at 6 °C in the four water types were determined to be 237, 95, 173, and 233 days, respectively, and the half-lives at 22 °C were determined to be 46, 23, 18, and 30 days,

respectively. The study shows that degradation rates increase with pH and temperature, and are fastest in river water (ATSDR, 2008).

Photolysis studies of methyl parathion have been reported. A study examining the photo-degradation of methyl parathion in river and seawater at variable temperatures showed the half-lives to be 11 and 34 days, respectively (ATSDR, 2008). During photolysis in natural water, 50% of the original methyl parathion concentration was degraded in 8 days in the summer and 38 days in the winter. In a photolysis study of methyl parathion in fresh waters of Portugal, a half-life of 3 days in groundwater and a half-life of 4 days in river water were observed. The authors noted that the transformation products, which included methyl paraoxon, were more stable than the parent compounds studied (ATSDR, 2008).

Methyl parathion is of low persistence in the soil environment, with reported field half-lives of 1 to 30 days. A representative value is estimated to be 5 days. The rate of degradation increases with temperature and with exposure to sunlight. Due to its low residence time, soil binding affinity, and low solubility in water, it is not expected to be significantly mobile.

One of the most important factors affecting the mobility of methyl parathion in the environment is its strong adsorption to soils. One study showed that after a 49-day incubation, 54% of the initial applied methyl parathion remained in the soil (ATSDR, 2008). Factors affecting the adsorption of methyl parathion are organic matter content of the soil and sediment, and the cation exchange capacity of the soil. Values for organic-carbon normalized soil adsorption coefficients, Koc, in five soil types were determined by EPA and were found to average 496, equal to a log Koc of 2.7 (ATSDR, 2008). Estimates of log Koc, calculated from the octanol-water coefficient (Kow), solubility, and melting point data ranged from 2.93 to 3.47. McLean et al. estimated a lower Koc of 39, equal to a log Koc of 1.59 (McLean et al., 1988). More recently, a Koc of 5,100, equal to log Koc 3.7, has been reported. (HSDB 1999) These Koc values indicate that methyl parathion is moderately mobile to immobile in soil (ATSDR, 2008).

- Adsorption coefficient cm^3/g (Koc): 476
- Hydrolysis half-life (average days): 45.0
- Aerobic metabolism soil (average days): 12
- Anaerobic metabolism soil (average days): 1

Several studies have been conducted to measure methyl parathion in streams, rivers, and lakes. A U.S. Geological Survey (USGS) study of western streams detected methyl parathion in five river samples taken from four states during a 14-month period in 1970 and 1971. The amount of methyl parathion detected ranged from 0.04 to 0.23 μg/L. A later and more extensive USGS study analyzed water samples from major rivers of the United States four times yearly in the period of 1975 - 1985. Of the 2,861 water samples, 0.1% had detectable levels of methyl parathion. In a study of Arkansas surface waters, samples of lake and river/stream water were collected and analyzed over a three-year period. Of the 485 samples collected, methyl parathion was found in one river/stream sample at a maximum concentration of 3.5 μg/L (ATSDR, 2008).

Groundwater has also been surveyed for methyl parathion. In a study of well water in selected California communities, methyl parathion was not detected (detection limit of 5 ppb) in the 54 wells sampled, even though the insecticide had been used in the areas studied for over 15 years. An analysis of 358 wells in Wisconsin produced the same negative results. In a

sampling of California well water for pesticide residues, no methyl parathion was detected in any of the well water samples (ATSDR, 2008).

The typical surface water concentrations of methyl parthion is summarized in Table 1.8.

Table 1.8.Typical surface and groundwater concentration of methyl parathion

Type	Location	Minimum (µg/L)	Maximum (µg/L)	Mean (µg/L)	Source
Surface water	US	0.04	0.23		(Barnes et al., 2002)
Ground water	US			not detectable	(Barnes et al., 2002)

1.3.3.2.6. Phenol

Phenol is both a manufactured chemical and a natural substance. It is a colorless-to-white solid when pure. The commercial product is a liquid.

Small, single releases of phenol do not stay long in the air (usually half is removed in less than 1 day), and usually do not stay in the soil for long periods (usually completely gone in 2-5 days), but can stay in water for longer than 9 days. Phenol has been found in materials released from landfills and hazardous waste sites, and it has been found in the groundwater near these sites. Phenol is usually found in the environment below 100 parts per billion (ppb), although much higher levels have been reported. One ppb or less of phenol has been found in relatively unpolluted surface and ground waters.

Although phenol does not absorb light at wavelengths >290 nm, phenols react rapidly to sunlight in natural water via an indirect reaction with photo chemically produced hydroxyl radicals and peroxyl radicals; typical half-lives for hydroxyl and peroxyl radical reactions are on the order of 100 and 19.2 hours of sunlight respectively. The estimated half-life for the reaction of phenol with photo chemically produced singlet oxygen in sunlit surface waters contaminated by humic substances is 83 days (ATSDR, 2008).
Available data indicate that phenol biodegrades in soil under both aerobic and anaerobic soil conditions. The half-life of phenol in soil is generally less than 5 days, but acidic soils and some surface soils may have half-lives of up to 23 days. Mineralization in an alkaline, parabrown soil under aerobic conditions was 45.5, 48, and 65% after 3, 7, and 70 days, respectively (ATSDR, 2008).

Limited information on surface water concentrations of phenol is summarized in Table 1.9.

Table 1.9.Typical surface and groundwater concentration of phenol

Type	Location	Minimum (µg/L)	Maximum (µg/L)	Mean (µg/L)	Source
Surface water	US	0.08	0.4		(Lee et al., 2004)

1.3.3.3. Summary of Fate and Transport of Six Microconstituents

Estimates of removal half-life for each of the six selected microconstituents and typical removal were obtained from the various data sources and also by applying the estimation software EPIwin v3.12 from the US EPA. The software also contains a large database of literature values. If database records were found, these were compiled instead of using the

estimates. The results are show in Table 1.10. There is some variability and some of the data sources are even giving contradictory information.

It was difficult to obtain actual literature values for removal and degradation rates in groundwater. However, relative removal potential is estimated based on biodegradation, sorption and general degradation potential. Half-life constants in groundwater for degradable compounds are estimated based on information from degradation in soil. As a conservative estimate, the half-life in groundwater is assumed to be 10 times the degradation in soil. The properties of selected microconstituents for recharge modeling are summarized in Appendix B.

Half-life estimates can be converted into a first-order degradation rate or vice versa by the following conversion:

Half-life: $t_{1/2} = \ln 2 / k_{deg} \Rightarrow 0.6931 / k_{deg}$
Degradation rate: $k_{deg} = \ln 2 / t_{1/2} \Rightarrow 0.6931 / t_{1/2}$
Where:
$T_{1/2}$ = half-life [Time]
k_{deg} = rate constant [$Time^{-1}$]

From the six researched microconsitutens, three were chosen for modeling alongside a conservative tracer. The selected compounds were Sulfamethoxazole, phenol, and Triclosan based upon their photodegration, sorption, and biodegradation characteristics, as well as their detection as poart of this project.

Table 1.10. Estimated physical chemical properties, half-lives, and degradation constants

Compound	Log Kow Value[1]	Log Koc Value[1]	WWT removal (%)[1,2]	Ready Biodegradation[1]	Half-live[1]			
					Photolysis	Volatilization-Surface water	Total-Surface water	Total-groundwater
Sulfametho-xazole	0.89	3.2	1.88	No, Yes, aerobic activated sludge (Drillia et al., 2005), not biodegradable (Kjølholt et al., 2003)	2.7-6.6 hrs (Lam and Mabury, 2005)	9.75E+08 hrs	900 hrs	Insignificant
Triclosan	4.76, 4.8 (Samsøe-Petersen et al., 2003)	4.3	83.1	No, 432 hrs in soil (Ying et al., 2007)	10 days[6], 41 min (Reiss et al., 2002), Neglible (Reiss et al., 2002)	4.68E+04 hrs	1.44E+03 hrs, 504 hrs[6], 2.8 hrs Bio + photo (Morrall et al., 2004), 13 hrs (Samsøe-Petersen et al., 2003)	Moderate[3], 180 days[4]
Ibuprofen	3.97	2.6	28.72	No, Not readily[7], Degradable to some extent	No[6]	5534 hrs	360 hrs, 480 hrs[6]	Insignificant[3]
4 nonylphenol	5.76	4.8	99.88	No, Yes, 168 hours (Ying et al., 2003)	Indirect photolysis 10-15 hrs (Ahel et al., 1994)	27.08 hrs	360 hrs	Moderate[3] 70 days[4]
Methyl-parathion	2.86, 2.93-3.47 (McLean et al., 1988)	2.7, 1.59 (Lam et al., 2004), 3.7[6]	28.22	No, Yes, 2,280 - 5,688 (hrs) at 6 °C, 432 – 1,104 (hrs) at 22°C[5]	Yes[5], 192 hrs summer 912 hrs winter 72 -96 hrs River[5]	9500 hrs	900 hrs, 100 % removal 336-720 hrs[5]	Moderate[3], 50 days[4]
Phenol	1.46	2.4, 1.21-1.96[5]	92.15	Yes, Yes < 120 hrs[5]	1,992 (hrs)[5]	1707 hrs	360 hrs, 216+ hrs[5], 168+ hrs[5]	Readily[3,] 25 day[4]

Notes:
1. Unless specified, all values were estimated from EPIwin software v3.12 US. EPA
2. WWT removal: Waste water removal percentage including removal by volatilization, biodegradation and sorption
3. Relative degradation estimate based on physical-chemical properties and bio degradation
4. Half live in groundwater is estimated based on information from degradation in soil. As a conservative estimate the half-life is assumed to be 10 times the degradation in soil
5. The Agency for Toxic Substances and Disease Registry: http://www.atsdr.cdc.gov
6. Hazardous Substance Data Bank http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB
7. ESIS: European chemical Substance Information System (>RAR) http://ecb.jrc.it/esis/

CHAPTER 2
MATERIALS AND METHODS

2. MATERIAL AND METHODS

2.1. Pilot Treatment Units

Three membrane treatment processes were uses in this study. Two pilot treatment units (MBR/RO and DNF/UF/RO) at Plantation, FL have been defined previously (Hazen and Sawyer, 2007) and are reviewed here. Another membrane system (IMANS^{TM}) tested on the bench top at Orange County, CA is described here as well. Five rounds of sampling were conducted. The first two rounds of sampling were performed on MBR/RO system on 10/29/2007 and 11/26/2007. The following three rounds of sampling were performed on DNF/UF/RO system on 1/14/2007, 1/31/2008, and 2/21/2008. The sampling for IMANS system also happened on 2/21/2008.

2.1.1. MBR/RO

The treatment process consists of primary clarification, MBR, and RO. The MBR system, Zenon ZeeWeed 500, is manufactured by GE Water & Process Technologies. It consists of an activated sludge basin and an UF membrane system. The nominal pore size of the UF membrane is 0.04 μm. The RO machine, Osmonics E4H-16K-DLX, is manufactured by GE Water & Process Technologies. The spiral wound polyamide thin film composite membrane (4820 ULP) used in the RO system is manufactured by Koch Membrane Systems.

During the first sampling event on 10/29/2007, the flow rate of MBR system was 10 gpm with a 2gpm bleeding system. The mixed liquor suspended solids (MLSS) in MBR system was 5330 mg/L. Flux in the MBR system was 22.25 gallon flux per day (gfd). The solid retention time (SRT) of the MBR system was 13 days and hydraulic retention time (HRT) was 6.24 hours. The internal recycle ratio from aerobic to anoxic phases in the MBR system was 4. The flow rates of RO influent, RO effluent, and RO brine were 8 gpm, 4 gpm, and 4 gpm respectively. The dissolved oxygen (DO) in the aeration tank was 1.74 mg/L. Water temperature was 29.2 °C. Air scour rates of MBR system were between 18 and 20 cubic feet per minute (cfm). RO system was operated for 10 minutes then backwashed for 30 seconds. Membranes were cleaned once every 20 minutes. The operational conditions for the second sampling event on 11/26/2007 were the sameas the first sampling event, except that MBR flow was 12.4 gpm, MLSS was 2670 mg/L, MBR flux was 22.13 gpd, DO was 1.97 mg/L, amd temperature was 28.3°C.

2.1.2. DNF/UF/RO

The treatment process consists of primary clarification, activated sludge secondary treatment, secondary clarification, tertiary clarification, denitrification filtration (DNF), UF, and RO. The Denitrification system was elimi-NITE Denitrification System manufactured by ITT Leopold. The UF (Zenon ZeeWeed 500) and RO system (Osmonics E4H-16K-DLX) are the same as those used in the MBR/RO process.

During the third sampling event on 1/14/2008, the flow rate of the DNF system was 16 gpm. The nitrate concentration in DNF effluent was 2.70 mg/L. Water temperature was 25.8°C.

The methanol concentration in the DNF system was 35 mg/L. The flow rates of UF influent, UF effluent, and UF brine were 7.2 gpm, 3.4 gpm, and 3.8 gpm, respectively. The flow rates of RO influent, RO effluent, and RO brine were 7.8 gpm, 3.9 gpm, and 3.9 gpm, respectively. During the fourth sampling event on 1/31/2008, the flow rate of the DNF system was 12 gpm. The concentration of methanol in the DNF system was 48 mg/L. The concentrations of nitrate in DNF influent and DNF effluent were 12.9 mg/L and 1.9 mg/L, respectively. Water temperature was 25.0°C. The flow rates of UF influent, UF effluent, and UF brine were 10 gpm, 7.4 gpm, and 2.6 gpm, respectively. The flow rates of RO influent, RO effluent, and RO brine were 9.6 gpm, 3.8 gpm, and 3.8 gpm, respectively. During the fifth sampling event on 2/21/2008, the flow rate of the DNF system was 12 gpm. The concentration of nitrate in DNF influent was 13.7 mg/L. The flow rates of UF influent, UF effluent, and UF brine were 12 gpm, 10 gpm, and 2 gpm, respectively. The flow rates of RO influent, RO effluent, and RO brine were 9.5 gpm, 3.9 gpm, and 4.0 gpm, respectively.

2.1.3. IMANS

Carollo contributed time, materials, and cash to cover all aspects of benchtop testing of membrane processes to supplement this project. This additional effort was intended to provide a comparison of treatment by membranes with and without the biological secondary treatment component. Briefly, the IMANS™ approach (Figure 1) involves conventional primary settling of the wastewater, followed by UF. The UF step separates the soluble and residual insoluble organic material. Solid material removed by the UF membranes may be returned to anaerobic digesters with the solids from primary clarification. The UF product stream containing soluble organic material is treated in a RO or NF process. For this project, the RO process was utilized.

The RO permeate is a high-quality water ready for final disinfection and use, while the RO brine contains rejected salts and concentrated soluble organic material. The organic-rich RO concentrate stream, which is free of suspended material, stabilized in a high-rate anaerobic digestion process. The concept potentially eliminates the need for conventional secondary activated sludge treatment.

2.2. Sampling Locations and Sample Handling

There were five sampling events spaced over three months of pilot system operation. Figure 1-1 outlines the sampling locations in the AWT trains. The first two sampling events were conducted on the MBR/RO train and the third, fourth, and fifth sampling events were conducted on the UF/RO train. The final sampling event also included the benchtop testing of the membrane only (IMANS™) process and the sampling of canal water to provide some perspective on background water quality.

To reduce the potential for contamination, sample collectors were requested to be non-smokers, wear gloves during sample collection, and refrain from using lotions, perfumes, sunscreen, and lip balm prior to sample collection (Rosen, 2007). H&S staff collected all samples from the pilot systems with assistance and coordination by Carollo staff. All samples were hand delivered or shipped on ice to the appropriate laboratories for analysis via overnight delivery. The sampling and analysis protocols for each test are further detailed in the following sections.

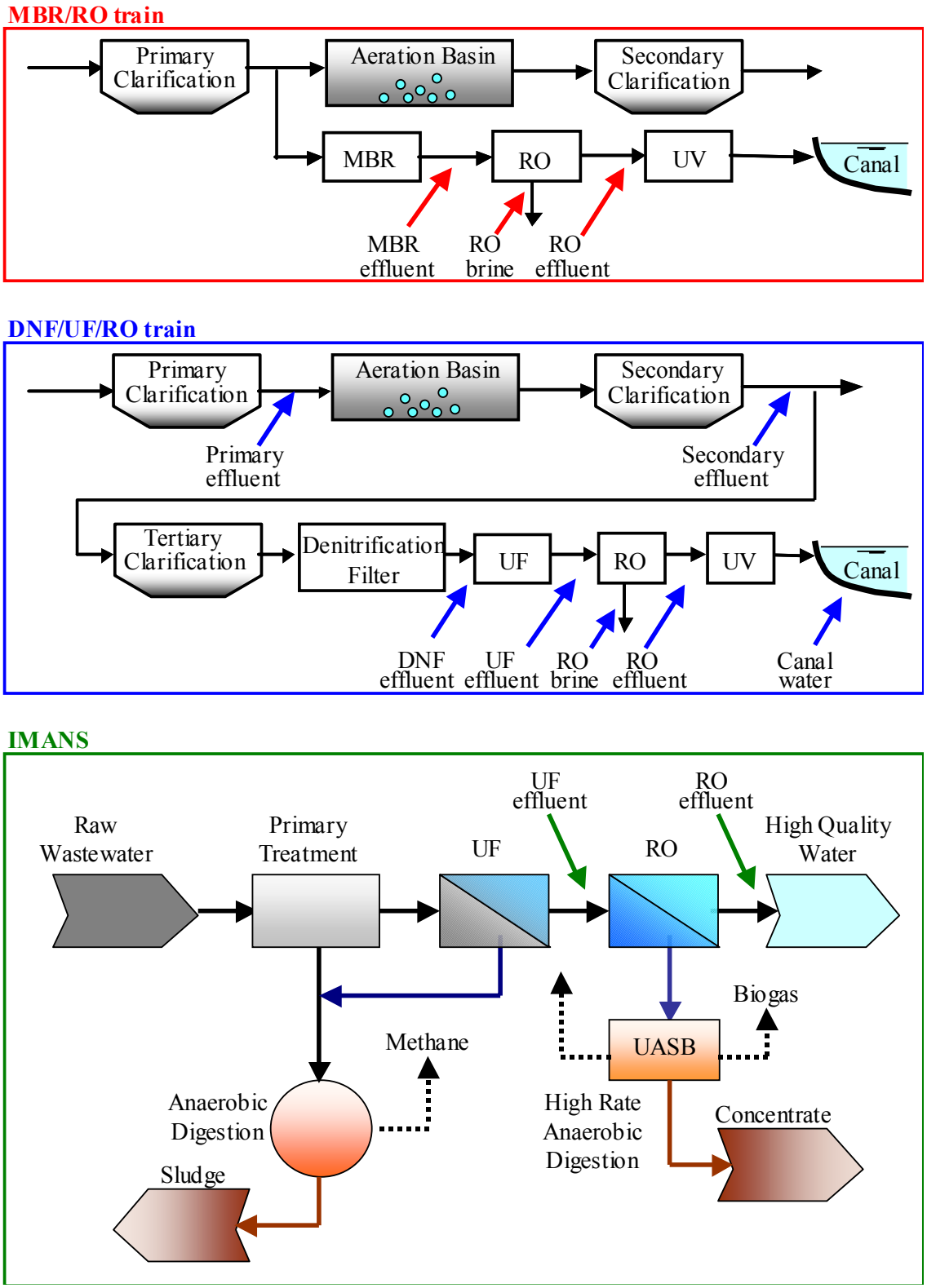


Figure 1-1. Process scheme and sampling locations.

2.3. Water Quality Measurements

Water quality parameters evaluated in samples were pH, total suspended solids (TSS), biochemical oxygen demand (BOD), total dissolved solids (TDS), and particle size distribution (PSD). Three 1-liter samples were collected for each sampling location for TSS, BOD and TDS analysis by the Plantation WWTP analytical laboratory. One 500-milliliter sample was collected at each location for PSD analysis by Carollo Engineers. These results were used to evaluate the efficiency of the advanced treatment process in removing solids and BOD and improving water quality.

2.4. Microconstituent Testing

Microconstituent concentrations were measured in the RO effluent and RO brine for the MBR/RO train, primary effluent, secondary effluent (secondary clarifier effluent), DNF effluent, RO effluent, and RO brine for the UF/RO train, and UF effluent and RO effluent for the IMANS™ system.

Microconstituent analysis was performed by Montgomery Watson Harza (MWH) Laboratories, following test method USGS mod 4 and LC-MS-MS. The analysis methods and detection limits of examined microconstituents are shown in Table 2.1.

Table 2.1.Analysis methods and detection limits of examined microconstituents

Microconstituents (ng/L)	Analysis methods	Detection limits
2,6-di-tert-butylphenol	USGS 4 MOD	10
4-Methylphenol	USGS 4 MOD	25
4-Nonyl Phenol	USGS 4 MOD	25
Acetaminophen	LC-MS-MS	1
Alpha Chlordane	USGS 4 MOD	10
Amoxicillin	LC-MS-MS	1
Bisphenol A (BPA)	USGS 4 MOD	25
Caffeine	LC-MS-MS	1
Caffeine	USGS 4 MOD	25
Carbamazepine	LC-MS-MS	5
Carbaryl	USGS 4 MOD	50
Chlorpyrifos	USGS 4 MOD	25
N, N-diethyl-m-toluamide (DEET)	USGS 4 MOD	25
Diazinon	USGS 4 MOD	25
Dieldrin	USGS 4 MOD	25
Estradiol	LC-MS-MS	1
Estrone	LC-MS-MS	1
Ethinyl Estradiol -17 alpha	LC-MS-MS	5
Fluoxetine	LC-MS-MS	1
Gemfibrozil	LC-MS-MS	1
Ibuprofen	LC-MS-MS	1
Iopromide	LC-MS-MS	5
Methyl Parathion	USGS 4 MOD	25
Phenol	USGS 4 MOD	100
Progesterone	LC-MS-MS	1

Microconstituents (ng/L)	Analysis methods	Detection limits
Sulfamethoxazole	LC-MS-MS	1
Tris(1,3-dichloro-2-propyl) phosphate	USGS 4 MOD	25
Testosterone	LC-MS-MS	1
Triclosan	LC-MS-MS	5
Triclosan	USGS 4 MOD	50
Trimethoprim	LC-MS-MS	1
Triphenylphosphate	USGS 4 MOD	25
Tris(2-butoxyethyl) phosphate	USGS 4 MOD	100
Tris(2-chloroethyl) phosphate	USGS 4 MOD	25

The isotope dilution method was used to prevent interference from the water matrix, as part of MWH Laboratory's analysis of microconstituent concentrations. Six-liter grab samples were collected from each sampling location in pre-preserved amber glass bottles provided by MWH Laboratories for sample analysis and quality control measurements.

Microconstituent concentrations in the MBR effluent in the MBR/RO train and UF effluent in the UF/RO train were determined through mass balance of microconstituent concentrations in the RO effluent and RO brine and the flow rates of product water and brine.

2.5. Toxicity Testing

To determine if various effluents had a potential to cause toxicity to aquatic organisms, standardized aquatic toxicity assays were performed. Biomonitoring with toxicity tests procedures for chronic 7-day static-renewal effluent exposures. Test organisms included the fathead minnow, *Pimephales promelas* and cladoceran, *Ceriodaphnia dubia.* Endpoints of toxicity tests included chronic survival and growth test of *P. promelas* and chronic survival and reproduction test of *C. dubia*. Five rounds of toxicity testing were conducted. The first three rounds of toxicity testing were performed by David Barber at the University of Florida, and the last two rounds of toxicity testing were performed by Golder Associates and Hydrosphere Research. Seven gallon samples were collected from each sampling location and shipped on ice overnight to the appropriate toxicity laboratory. The RO effluent samples were stabilized prior to toxicity testing, by adding salts to mimic the conductivity and chemistry of the control water, similar to the methods used in WERF Report 01-HHE-4A (Schlenk et al., 2007).

For the first sampling event, exposures for the chronic 7-day test using *P. promelas* were conducted in glass vessels filled with 250 ml of effluent. Four replicates, with each replicate containing eight *P. promelas* (24 hr old), was used for every treatment (effluent dilution) and control. Larval *P. promelas* were purchased from MBL Aquaculture, Sarasota, Florida. Test results were based upon survival at the end of 7 days. Daily feeding consisted of approximately 0.1 ml of newly hatched *Artemia*. A minimum 80% survival of the control organisms was required. Exposures for the chronic 7-day test using *C. dubia* were conducted in 250 ml glass containers filled with 50 ml of effluent. Four replicates, containing three *C. dubia* neonate (less than 24 h old), were used for each effluent dilution and control. The neonates were transferred from third-brood laboratory stock cultures. Daily renewal of the tests with effluent was conducted after the first reproduction occurred. Daily feeding of the tests included 0.1 ml each of laboratory-cultured YCT (yeast, cereal, and trout chow) per test chamber. A minimum 80% survival of the control organisms was required. Test results were based upon survival and reproduction. All tests were conducted at 25±2°C with 16:8-h light/dark photoperiod. All control and dilution water was laboratory constituted moderately

hard water (conductivity 408 µ Siemens and hardness 102 mg/l). The range of dissolved oxygen for all test chambers was consistently between 5.4 and 8.0 mg/L throughout the test duration.

For the second and third sampling events, *P. promelas* toxicity assays were conducted as above. *C. dubia* assays were conducted with 10 replicates per treatment. Each replicate contained a single individual in 30 ml of test water. Dilution water for these tests was laboratory constituted moderately hard water with a conductivity of 1190-1300 µ/siemens and a hardness of 312 mg/L as based on the AWT facilities' RO effluent stabilization recipe for dilution water and control water. Control and dilution water contained selenium as recommended by EPA guidelines.

Values for survival and reproduction were obtained using a hypothesis test approach with one way ANOVA and Dunnett's Procedure (EPA, 1994). Tests for normality and homogeneity of variance included Shapiro–Wilks and Bartlett's Test, respectively. The response used in the analysis was either the number of animals surviving at each test concentration, or with respect to reproduction data, the number of young produced per adult female. Reproductive success was determined by taking the total number of young produced until the time of death of the adult or the end of the experiment, whichever came first. The mean number of live young produced per adult female for each effluent concentration provided a combined measure of the effluent's effect on both mortality and reproduction (EPA, 1994).

For the fourth and fifth sampling events, the 7-day chronic static renewal definitive bioassays conducted with the *P. promelas* and *C. dubia* were conducted according to the USEPA standard method EPA-821-R-02-013 (EPA, 2002). The water used for acclimation, culture, and dilution during the testing was moderately hard reconstituted freshwater (MHR) prepared according to EPA methods (EPA, 2002). For the *C. dubia* and *P. promelas* tests, serial dilutions were prepared using the samples and MHR. These dilutions were 0 (controls), 6.25, 12.5, 50, 75, 100 percent sample. The *C. dubia* tests were conducted with one organism per replicate and 10 replicates per concentration. The *P. promelas* tests were conducted with 10 organisms per replicate and 4 replicates per concentration. Samples were stored at less than 4 °C in a cold room until test initiation. The sampels were warmed to 25 °C prior to test initiation. The warmed samples were checked for total residual chlorine using a Chlorimeter (HACH DR/890), method 8167 for Total Chlorine, which is equivalent to USEPA method 330.5 for wastewater and Standard Methods 4500-Cl G for drinking water. Similarly to the first three tests, the RO effluent samples were stabilized prior by adding salts to mimic the conductivity and chemistry of the control water, as described in WERF Report 01-HHE-4A (Schlenk et al., 2007). UF samples and primary effluent samples were not altered in any fashion. The *C.dubia* and *P. promelas* tests were monitored daily for survival, reproduction (*C. dubia* only) temperature, pH, dissolved oxygen, and conductivity. The *C. dubia* and *P. promelas* were fed prior to test initiation and at every daily renewal. *P. promelas* was fed *Artemia* nauplii twice daily and *C. dubia* was fed YCT and the green alga, *Selenastrum capricornutum* daily. All tests were conducted at 25±1°C. The range of dissolved oxygen for all test chambers was consistently between 5.0 and 8.9 mg/L throughout the test duration, and the pH range was 7.6 to 8.6. Standard F-tests and T-tests were conducted to determine if each sample's data was significantly different from the respective control data. For both the F-tests and T-tests, an alpha of 0.05 was used. The reference toxicant test was conducted with potassium chloride to document test organism health. All reference toxicant tests showed that the test organisms were of normal sensitivity.

2.6. E-Screen Bioassay

To complement the toxicity testing and microconstituent analysis, E-Screen bioassays were conducted to demonstrate the extent to which the various advanced treated effluents possess endocrine disrupting potential as measured by an *in vitro* assay. The E-Screen used MCF-7 cells, a breast cancer cell line, that proliferates in responses to estrogenic activity. This bioassay is an *in vitro* assay and can demonstrate whether compounds in the various advanced treated effluents bind to a hormone receptor and elicit a response. All E-Screen bioassays were conducted at the Wisconsin State Laboratory of Hygiene (WSLH) by incubating MCF-7 cells in media containing extracts of the collected samples. Two 1-liter samples of each advanced treated effluent were collected in amber glass bottles provided by WSLH. MCF-7 cells were incubated in media with no sample extract as a negative control and in media dosed with estradiol as a positive control. Tests were run concurrently with samples of known estrogen concentrations. Following incubation, cell proliferation was measured by the sulphorhodamine protein assay, which determines the total number of cells through the total protein content. Each set of E-Screen bioassay was conducted alongside an estradiol standard curve, which consists of multiple concentrations of estradiol in the cell media. The cell proliferation results from the extracted treatment process samples were compared to a standard curve to determine the estradiol equivalents of the sample water. This assay does not indicate specifically what compounds are causing the estrogenic activity. The limit of detection is 0.027 ng/L and samples below this are reported as ND. The limit of quantification is 0.052 ng/L and activities below this, but higher than 0.027 are reported at < LOQ. Standard deviations reported are of the triplicate wells. Each sample is run with a positive control to ensure the sample itself is not interfering with the growth of the cells. Interference is set at <80% of the positive control growth.

2.7. Yeast Estrogen Screen Bioassay

Two *in vitro* assays are commonly found in the literature, the E-screen and the Yeast Estrogen Screen (YES). For this project, both assays were performed to potentially provide some correlation of the information gathered as part of this project with YES information gathered as part of other projects (particularly WRF 02-009, *Innovative Treatments for Reclaimed Water*). In the YES assay, yeast cells were transformed to contain human estrogen receptors, and, similar to the E-Screen, can indicate potential estrogenic activity of the sample water. In this test, yeast cells that have been transfected with the human estrogen receptor and a β-galactosidase reporter plasmid were exposed to an extract of the water sample. Compounds in the water extract that bind to the estrogen receptor will cause the cell to produce β-galactosidease, which can be measured spectrophotometrically. The YES assays were conducted at the WSLH. Two 1-Liter samples of each process sample were collected in amber glass bottles provided by WSLH. At WSLH, transformed yeast cells were grown to a specific density and exposed to diluted sample extracts. Sample extracts were run concurrently with samples of known estrogen concentrations. The β-galactosidease activity of the unknown sample was compared with the activity at the known estrogen concentrations and the results of the unknowns were reported as estradiol equivalents in ng/L. This assay does not indicate specifically what compounds are causing the estrogenic activity. The limit of detection depends on the concentration of extract used and for these samples was generally 0.20 ng/L and samples below this were reported as ND. Standard deviations reported are of the triplicate wells. The optical density was measured on each to ensure the density of the yeast cells was not reduced due to toxicity of the extract. The results from the YES bioassay

allowed for comparison with results from the E-Screen and the vitellogenin and steroid assays.

2.8. Fathead Minnow Vitellogenin and Steroid Assays

Fathead minnow vitellogenin (Vtg) assays and steroid immunoassays were conducted to demonstrate whether the fish are potentially impacted by exogenous estrogenic substances from the various treated effluents. Vtg induction in male fathead minnows is an *in vivo* test that can complement the microconstituent analysis and *in vitro* E-screen and YES assays. The measurement of steroid hormones in the blood of the fish, including testosterone and estradiol, also provides an *in vivo* measure of potential impact. The Vtg assays and steroid immunoassays were conducted by Nancy Denslow's laboratory at the University of Florida. Effluents were sent to the University of Florida for fathead minnow exposures. One 20-gallon sample of each effluent was collected and hand delivered on the day of collection. Only male fathead minnows were used in the exposures. Prior to the exposures, the fathead minnows were acclimated to the water and tanks, and fed a formulated trout diet at 1% of their body weight. The male fathead minnows were subjected to 7-day semi-static exposures in four separate tanks per exposure group. Each treatment consisted of three-12 liter glass aquariums containing 3 adult male fathead minnows and 4 liters of exposure solution. Exposures were conducted for 7 days with a 90 percent water change daily. The fathead minnows were also exposed to a negative control water and a positive control (5 ng/L ethynylestradiol) for each exposure set. On the 8th day of exposure, male fathead minnows were anesthetized with MS-222 (100 mg/L buffered with sodium bicarbonate). Then, blood was collected from the caudal sinus into heparinized microcentrifuge tubes. Plasma was obtained by centrifuging blood samples at 1000 x g for 5 minutes. The plasma was collected and split between two tubes, one for Vtg analysis, and one for steroid analysis. The plasma was stored at -80º C until Vtg and steroid assays were performed.

The fathead minnow plasma Vtg were measured using the homologous enzyme-linked immunosorbent assay (ELISA) developed specifically by Nancy Denslow's lab and the University of Florida - Hybridoma Core (Denslow et al., 1999; Hemming et al., 2001). Specifically, concentrations of plasma Vtg were determined by direct Enzyme-Link Immunosorbent Assay (ELISA) using the monoclonal antibodies (mAb) 2D3 that is specific for carp but cross reacts well with FHM Vtg. The plasma samples were diluted 1: 100 and 1:10,000 with 10mM phosphate, 150mM NaCl, 0.02% azide, 10 KIU/mL Aprotinin, pH 7.6 (PBSZ-AP). FHM vtg standards (0, 0.005, 0.01, 0.02, 0.04, 0.06, 0.08, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0 µg/mL) containing 1:100 and 1:10,000, male plasma (in PBSZ-AP) were added to account for matrix effect. Samples and standards were loaded onto a 96-well ELISA plate in triplicate and stored overnight at 4ºC in a humidified container. The following day the plates were washed four times with PBSZ and then blocked with 1% BSA in 10mM Tris, 150mM NaCl, 0.05% tween, 0.02% azide, 10 KIU/mL Aprotinin, pH 7.6 (1% BSA/TBSTZ-AP) for 2 h at room temperature. The plates were rewashed with PBSZ (4 times) and the monoclonal antibody was loaded into wells on each plate. The lowest dilution (1:100) was probed with 1µg/mL of the mAb and the higher dilution of 1:10 K with 0.1 µg/mL. After the addition of the mAb, the plates were stored at 4ºC overnight in the humidified container. The following day the plates were washed and the biotinylated secondary antibody (goat anti mouse IgG-biotin) was added to each well at 1:1000 dilution in 1% BSA/TBSTZ-AP and incubated at room temperature for 2 h. The plates were washed, and strepavidin-alkaline phosphatase was added at 1:1,000 dilution in 1% BSA/TBSTZ-AP and incubated for 2 h at room temperature. After a final wash of the plates, the color was developed by adding 1 mg/mL p-nitro-phenyl phosphate in carbonate buffer (0.03M carbonate, 2mM $MgCl_2$, pH 9.6) and the color was

measured using an ELISA plate reader (SpectraMax Plus384, Applied Biosystems) at 405 nm. Concentrations of the unknowns were determined from the standard curves. The detection limit for FHM Vtg is 0.5 mg/L. All assays were performed in triplicate and reported as the mean of the three measurements. The coefficient of variation was <10% for all samples analyzed. Inter and intra-assay variability was routinely measured by analyzing controls on several plates and different runs was found to be <10%, and <5%, respectively.

The steroids were quantified by radioimmunoassay as previously described (Jensen et al., 2001). For testosterone analysis, samples were thawed on ice and 10µL of plasma was placed into 12 x 75 mm borosilicate glass test tubes. 90µL of buffer (0.1M phosphate, pH 7.6 containing 0.1% gelatin, phos-gel buffer) was added to allow efficient phase separation during extraction and samples were vortexed briefly. Samples were extracted by adding 1 mL of n-butyl chloride to each tube and vortexing for 1 minute. Samples were then centrifuged gently to separate organic and aqueous phases and the upper organic phase was transferred to a new 12 x 75 mm borosilicate glass tube. Samples were extracted a second time and the organic phases combined. Samples were evaporated to dryness under a stream of nitrogen and reconstituted in 100uL of phos-gel buffer containing 0.5% RIA grade bovine serum albumin. Samples were capped and placed on an orbital shaker overnight at 4°C to ensure optimal reconstitution. Recovery of testosterone using this method is typically 90% or greater based on recovery of ^{3}H-testosterone. Testosterone analysis was performed by Enzyme Linked Immunosorbent Assay (ELISA) using a kit for testosterone manufactured by IBL America (Minneapolis, MN). Standards were prepared in steroid-free serum provided with the kit and ranged from 0.1 to 6 ng/ml. R^2 values for the standard curve were greater than 0.99. Values of testosterone in the samples were determined from the standard curve and were multiplied by 10 to account for dilution of the sample. Up to 7 male fish in each treatment were analyzed. The number analyzed varied due to mortality, accidental inclusion of females and low volumes of plasma for some fish.

2.9. Recharge Modeling

As detailed previously, the fate and transport of select microconstituents from a point of hypothetical discharge through surface water canals and into the aquifer was modeled by DHI Water & Environment Inc. (DHI). Both a hydrodynamic model and a water quality model were developed. The model domain, river network, and wellfield locations are shown in Figure 2-2.

The hydrodynamic model for the City of Plantation AWT pilot study was extracted from the larger Broward County Baseline Model (BLM). The hydrodynamic model is an integrated surface-groundwater model that has been recently consolidated in 2006 (Broward County, 2006) from smaller integrated models by Camp Dresser & McKee Inc. (CDM) and DHI in 2002 and 2005 (Camp Dresser & McKee Inc., 2002; 2005a; b), and revised mainly to study alternative sources of water supply for the County (DHI, 2008a). The Advection-Dispersion (AD) solute transport routines in the MIKE SHE and MIKE 11 program are added to the hydrodynamic model. The MIKE SHE and MIKE 11 AD modules are capable of simulating bi-directional mass transfers between the groundwater and surface water components. The stability of this preliminary advection-dispersion model was tested by using a conservative tracer, which does not undergo degradation or adsorption. This hydrodynamic model serves as a base to evaluate the potential risk of well field groundwater contamination from the hypothetical point source discharge of highly treated reclaimed water. The details of the hydrodynamic model are included as Appendix C.

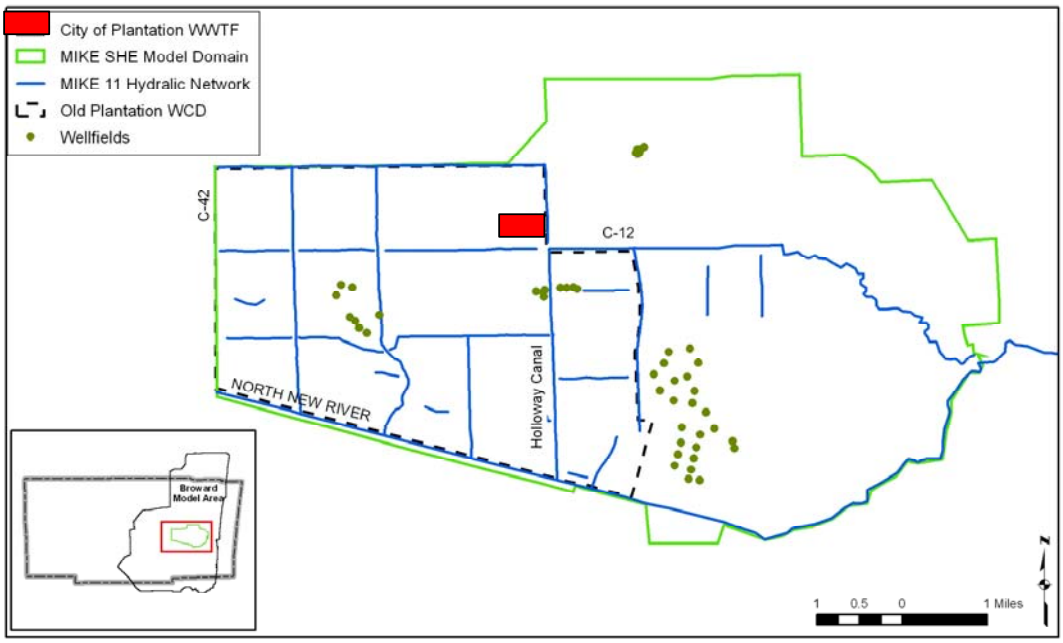


Figure 2-1. Plantation model domain, river network and wellfield locations.

For the water quality model, the ECO Lab template is used to simulate the various pathways of microconstituents in the canal water system. Three of the six microconstituents (Sulfamethoxazole, phenol, triclosan) from the literature review were selected for the water quality model, based on their properties of photodegration, sorption, and biodegradation, as well as their detection s as part of this project. The input parameters for the model were selected from the literature review and additional sources. The results obtained for the different microconstituents and for the conservative tracer are compared to evaluate the effect of the different degradation/removal processes in the surface water and groundwater system. The water quality model was carefully examined to ensure that results were reasonable. However, observation data is not currently available to perform model calibration.

CHAPTER 3
RESULTS AND DISCUSSIONS

3. RESULTS AND DISCUSSIONS

3.1. Water Quality Measurements

The results of the water quality analysis show that TSS in RO effluents were expectedly all below 1 mg/L and BOD_5 in RO effluents were all below 2 mg/L (Figures 3-1, 3-2, and 3-3), which were all below the values found in the canal water. The levels of TDS in RO effluents were below 19 mg/L in RO effluents, which is one order of magnitude lower than MBR or UF effluents (RO influents). Rejected TDS were concentrated in RO brines and removed from RO effluents. As shown in Figure 3-4, the average salt rejection rates (the percentage of TDS removed by the RO membrane) is 98.3%.

The pH values of all samples were close to neutral (7.0), except that the pH of RO effluents were all below 6.0 (Figure 3-5).

Turbidities of RO effluents, MBR effluents, and UF effluents were below 0.9 NTU, as shown in Figure 3-6. The turbidity of secondary effluent was a little higher (2.61 NTU), but the turbidity of all treated samples were lower than that of canal water (7.67 NTU).

The results of particle size distributions are shown in Figures 3-7, 3-8, and 3-9, respectively. Most small particles in MBR effluents and DNF effluents were removed by RO, and the resulting particle size distributions of RO effluents were not statistically different from those of distilled water. Some RO effluents had unexpectedly more particles than UF effluents, which could be caused by some regrowth downstream of the RO membrane or scale that could be flaking off of the permeate piping, or unclean sample ports that could have made the RO effluent particle concentration in the < 10 μm range higher than the UF particle concentration. The number of particles of all effluent samples in all size ranges were significantly lower than that of the canal water.

All of the water quality measurements suggest that the discharge of reclaimed water may not deteriorate general water quality of surface canals. A comparison of microconstituent values in the canal with the various effluents from the pilot testing is presented further on.

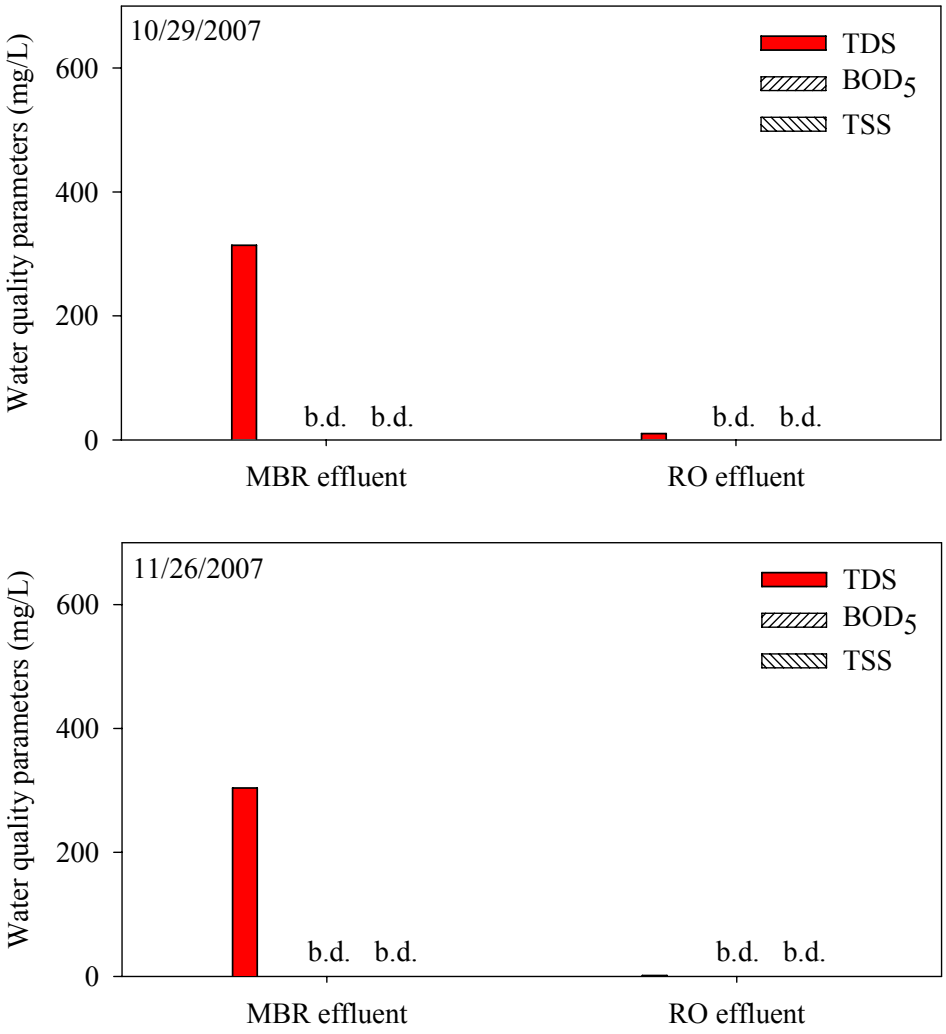


Figure 3-1.Results of water quality analysis of MBR/RO system.
b.d.: below detection limits (BOD_5 < 2 mg/L, TSS < 1 mg/L)

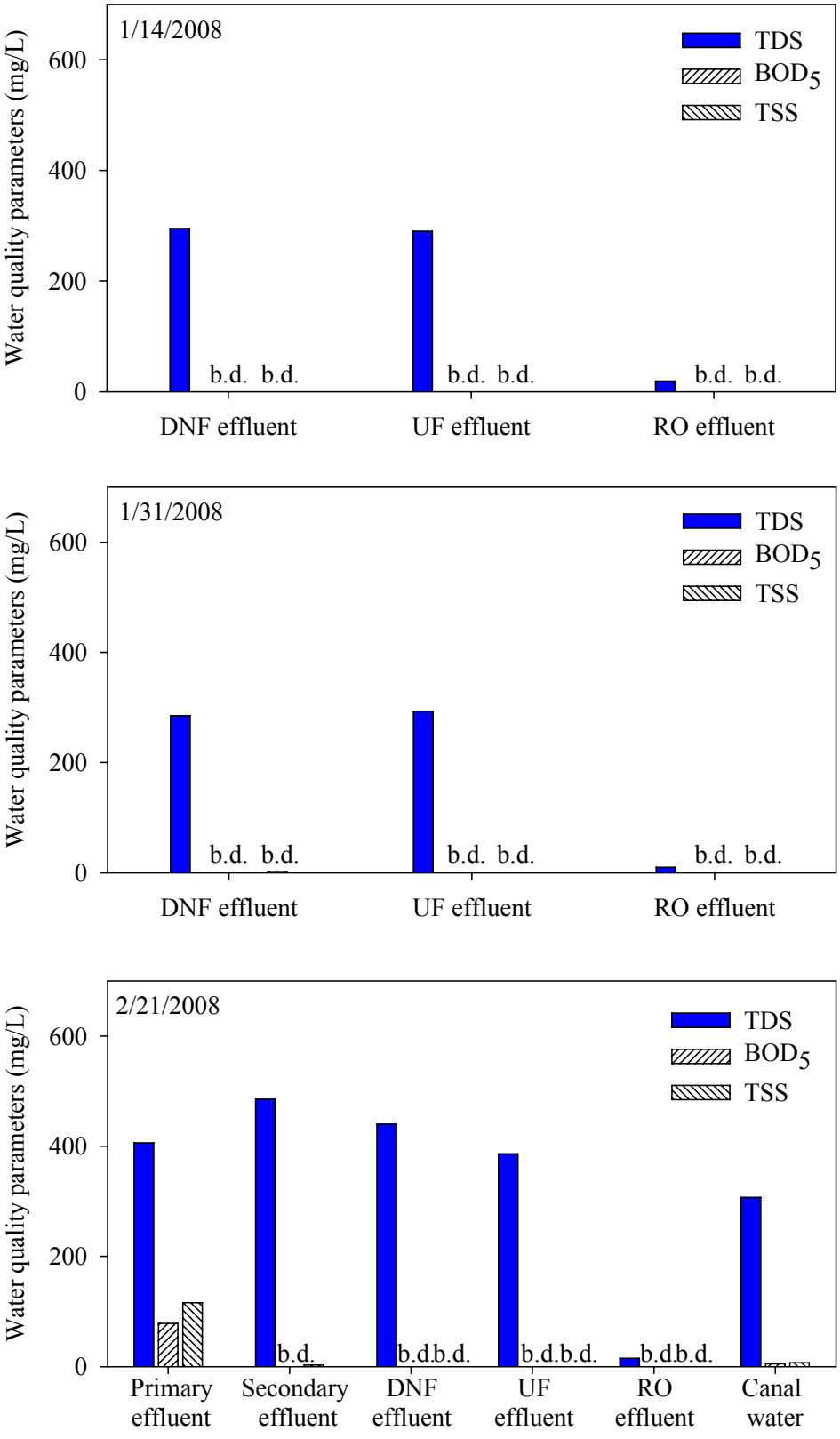


Figure 3-2.Results of water quality analysis of DNF/UF/RO system
b.d.: below detection limits (BOD_5 < 2 mg/L, TSS < 1 mg/L)

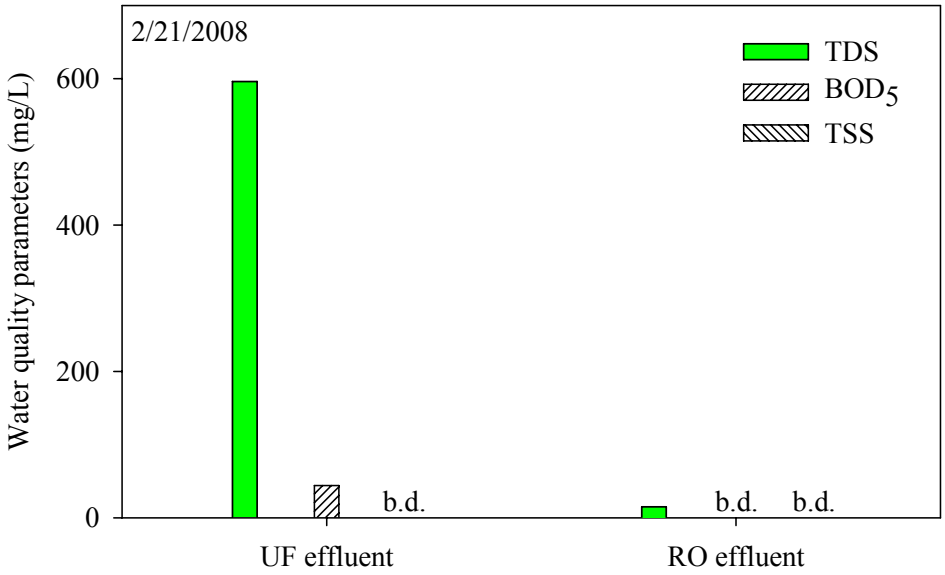


Figure 3-3.Results of water quality analysis of IMANS system
b.d.: below detection limits (BOD_5 < 3 mg/L, TSS < 10 mg/L)

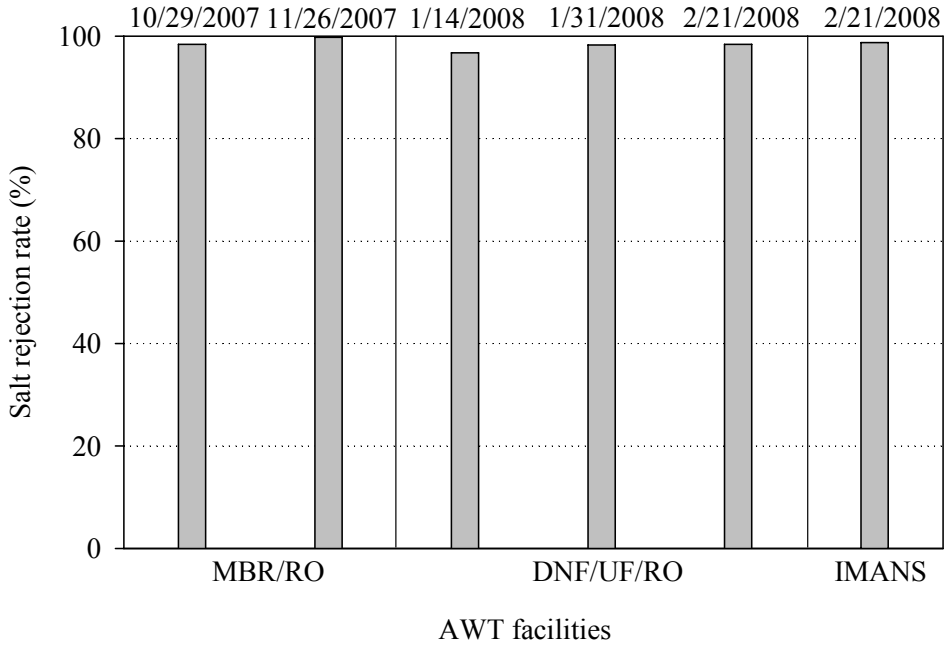


Figure 3-4. Salt rejection rates of MBR/RO system, DNF/UF/RO system, IMANS system

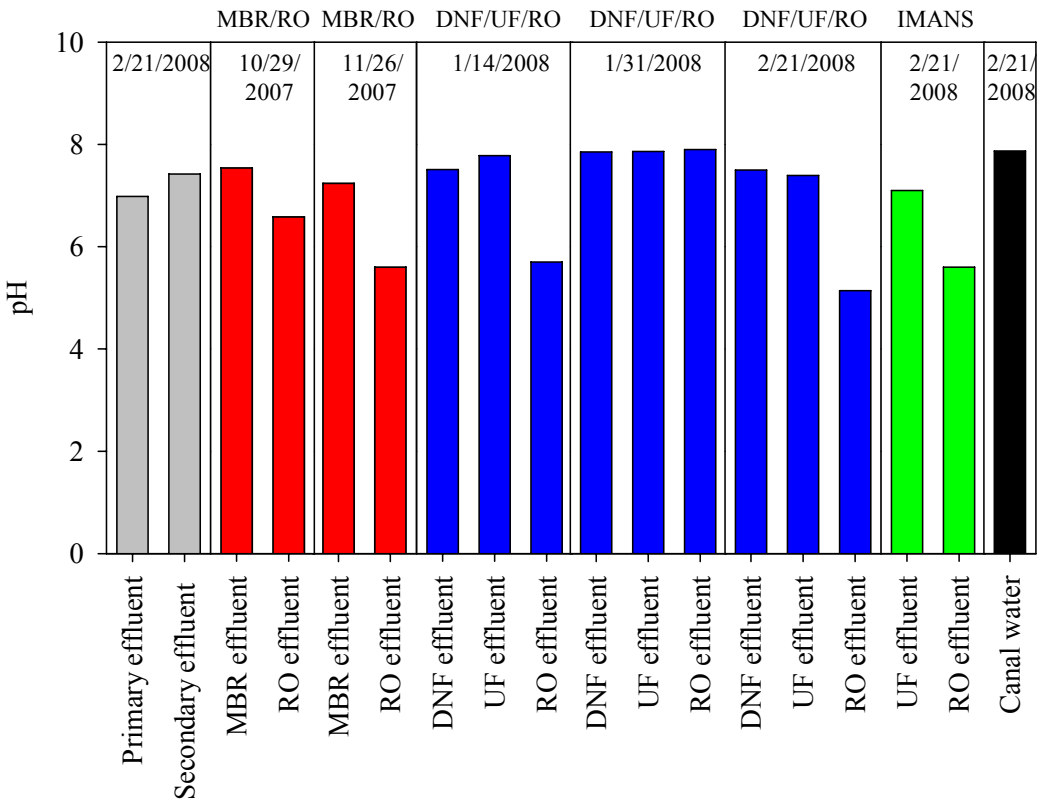


Figure 3-5.Results of pH of MBR/RO system, DNF/UF/RO system, IMANS system, and canal water

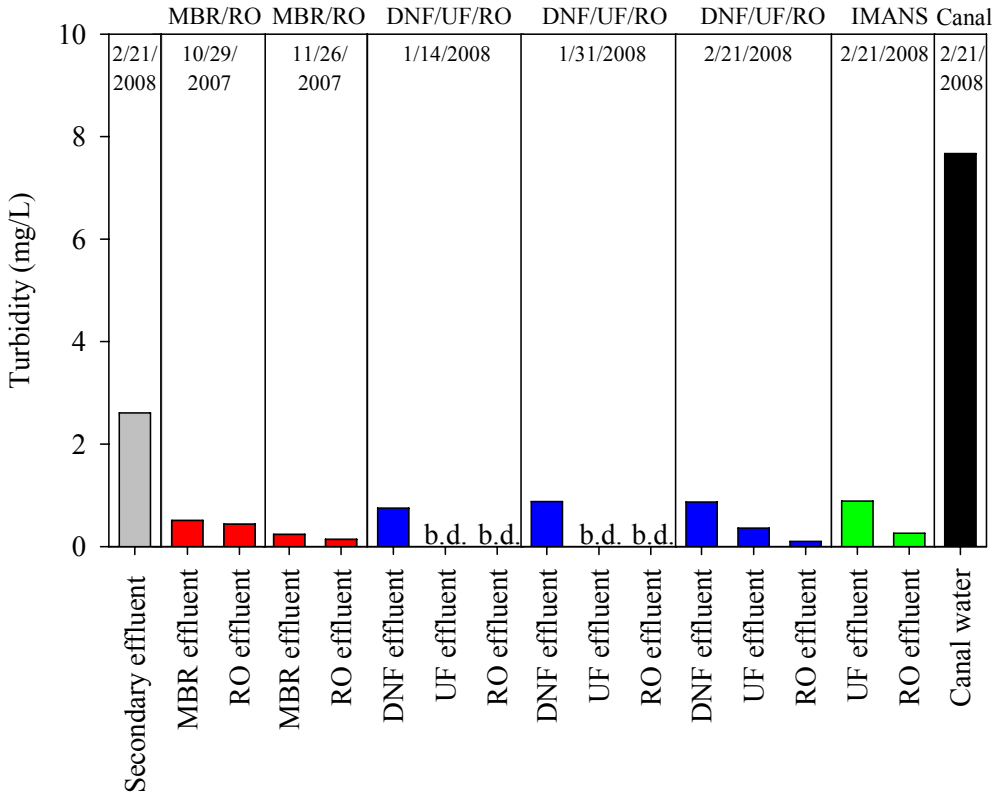


Figure 3-6.Results of Turbidity of MBR/RO system, DNF/UF/RO system, IMANS system, and canal water

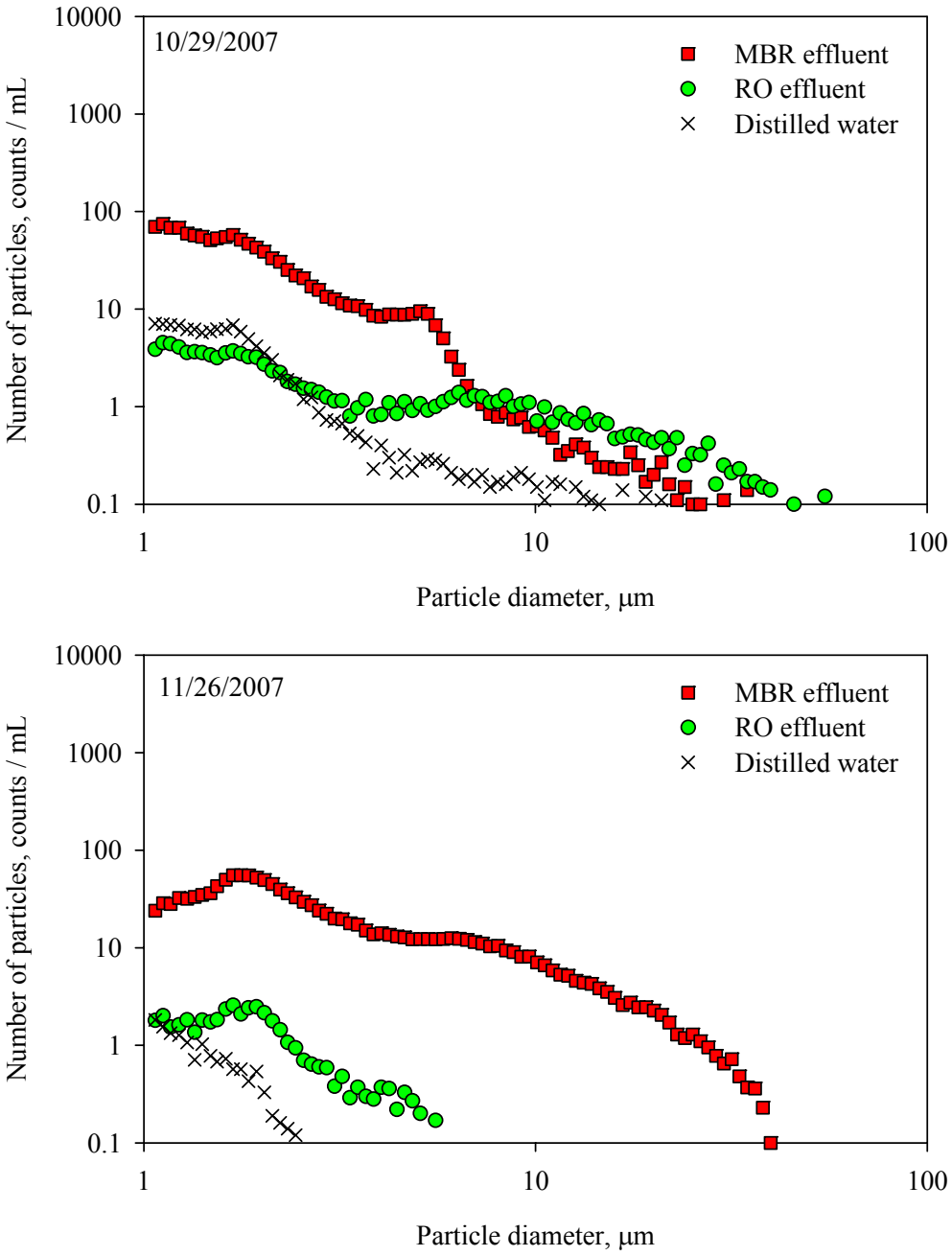


Figure 3-7. Particle size distribution of effluent in the MBR/RO system

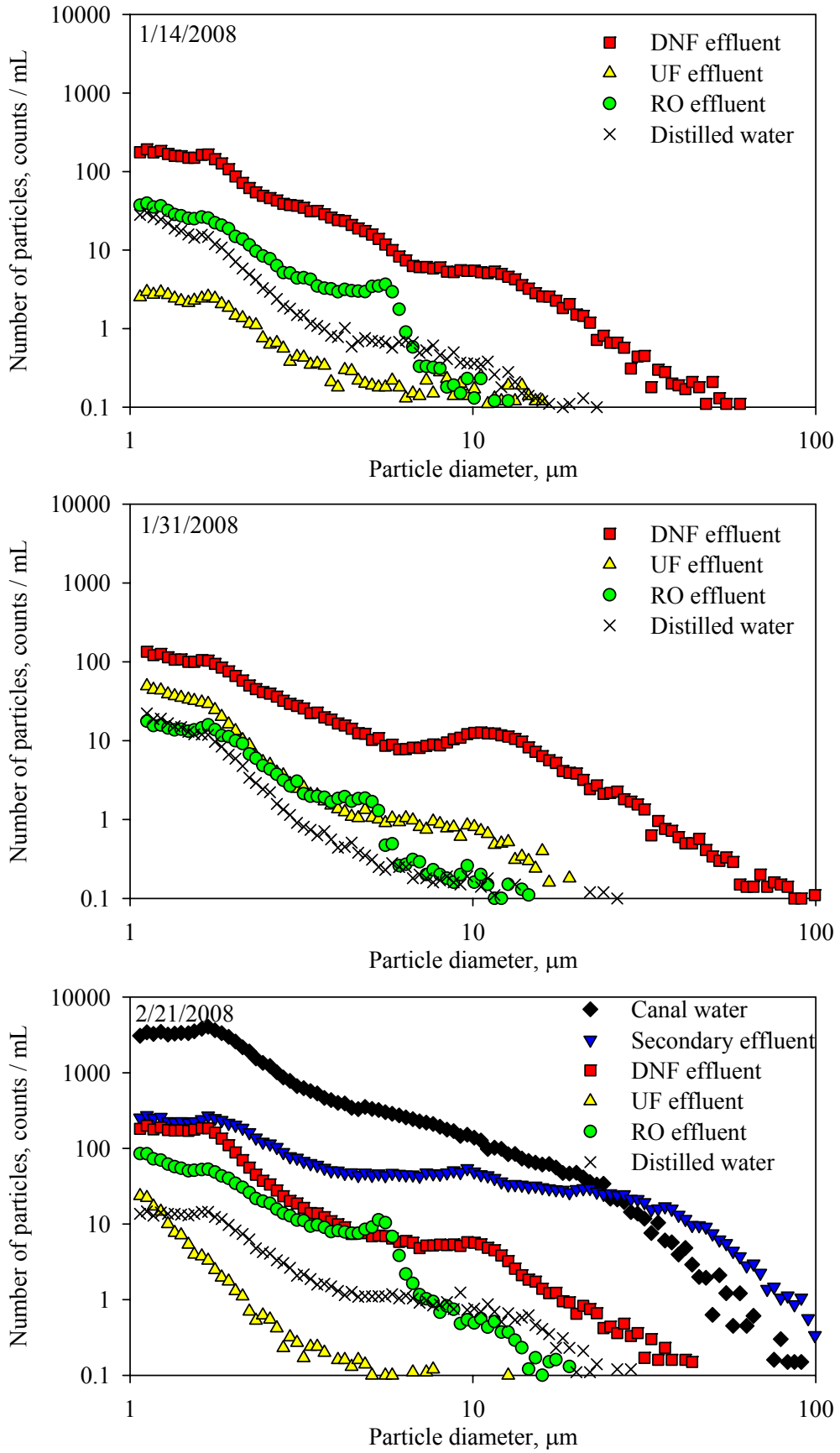


Figure 3-8. Particle size distribution of effluent in the DNF/UF/RO system

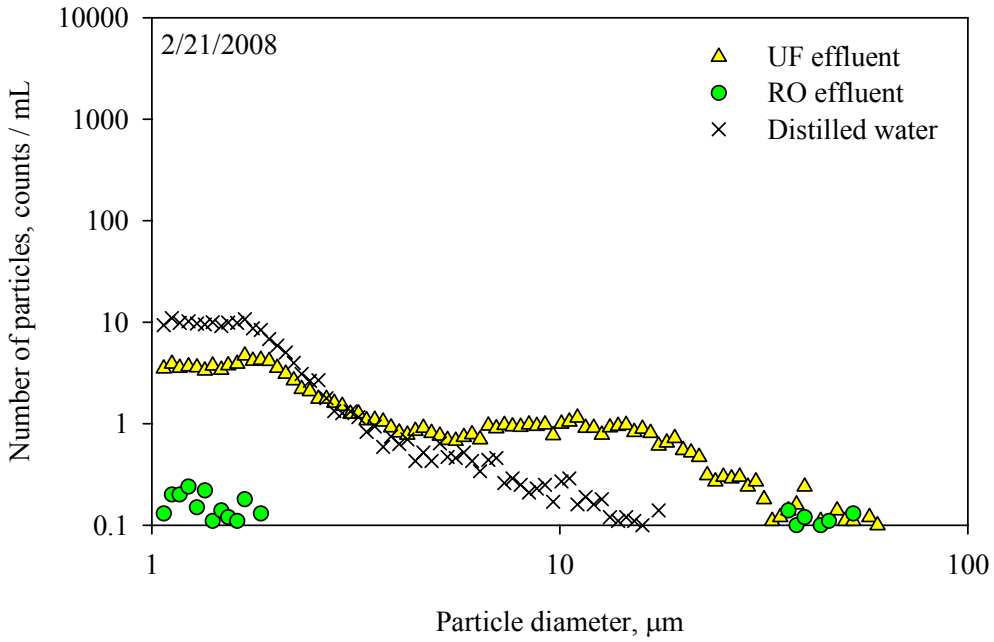


Figure 3-9. Particle size distribution of effluent in the IMANS system

3.2. Microconstituent Testing

As shown in Table 2.2, 15 and 19 out of 32 microconstituents were detected in the RO brine in the MBR/RO system and DNF/UF/RO system, respectively. Almost all microconstituents in RO effluent were below detection limits. All of these results indicated that RO system is effective at removing microconstituents. The rejection rates are more than 98%. These results were consistent with previous results that proved the effectiveness of removing microconstituents by RO membrane (Xu et al., 2005).

Duing the five rounds of sample analysis, bisphenol A (57 ng/L) was detected once and tris (1,3-dichloro-2-propyl) phosphate (TDCPP) (81 ng/L, 100 ng/L) were detected twice in RO effluent, however these detections were likely caused by sample contaminations. Bisphenol A is ubiquitous and can even be detected in lab distilled water, thus the detected bisphenol A is very likely a contamination during sampling or transportation. TDCPP is a chlorinated flame retardant that usually co-occurs with TCEP. TCEP was below detection limit while TDCPP was detected. TDCPP has a smilimar chemical structure as TCEP but has a much large size and is extremely well rejected (Bellona and Drewes, 2007). Similar to Bisphenol A, flame retardants are ubiquitous and anything out of plastic almost contains them. Therefore, it is very likely the detected TDCPP was caused by contamination, but not an indication of membrane failure.

Table 2.2. Concentrations of microconstituents

Treatment Trains	MBR/RO						DNF/UF/RO															IMANS	
Microconstituents (ng/L)	10/29/2007			11/26/07			1/14/2008				1/31/2008				2/21/2008							2/21/2008	
	RO influent[1]	RO effluent[3]	RO brine[2]	RO influent[1]	RO effluent[3]	RO brine[2]	DNF effluent	RO influent[1]	RO effluent[3]	RO brine[2]	DNF effluent	RO influent[1]	RO effluent[3]	RO brine[2]	Primary effluent	Secondary effluent	DNF effluent	RO influent[1]	RO effluent[3]	RO brine[2]	Surface water	RO influent	RO effluent
2,6-di-tert-butylphenol	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<1000	<10	<10	<10	<10	<10	<10	<10	<10
4-Methylphenol	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	**11300**	<25	<25	<25	<25	<25	<25	**30**	**37**
4-Nonyl Phenol	<25	<25	<25	<25	<25	<25	<25	**22.5**	<25	**45**	<25	**25.5**	<25	**51**	<2500	<25	<25	<25	<25	<25	<25	<25	<25
Acetaminophen	<1	<1	<1	<1	<1	<1	**2.9**	**2.2**	<1	**4.3**	<1	**2.5**	<1	**5**	**5400**	<1	<1	<1	<1	<1	<1	**6500**	**2300**
Alpha Chlordane	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<1000	<10	<10	<10	<10	<10	<10	<10	<10
Amoxicillin	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	<1
Bisphenol A (BPA)	**33.5**	<25	**67**	**40.5**	<25	**81**	<25	**26**	<25	**52**	<25	<25	<25	**35**	**5800**	**372**	**156**	**105.1**	NA*	**152**	**56**	<25	<25
Caffeine	**3.1**	<1	**6.1**	**6**	<1	**12**	**15**	**19**	<1	**38**	20	<1	<1	<1	**906000**	<1	**12**	**9.1**	<1	**18**	**152**	**61200**	**340**
Caffeine	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	**21000**	<25	<25	<25	<25	<25	**59**	**25000**	**139**
Carbamazepine	**43**	<5	**86**	**62**	<5	124	**106**	**102**	<5	**204**	**77**	**63.5**	<5	**127**	**176**	**57**	**53**	**56.7**	<5	**112**	<5	**98**	<5
Carbaryl	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<5000	<50	<50	<50	<50	<50	<50	<50	<50
Chlorpyrifos	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<2500	<25	<25	<25	<25	<25	<25	<25	<25
N,N-diethyl-m-toluamide	**27**	<25	**54**	**77**	<25	**154**	<25	**12.5**	<25	**25**	<25	**13.5**	<25	**27**	<2500	<25	<25	<25	<25	<25	<25	<25	<25
Diazinon	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<2500	<25	<25	<25	<25	<25	<25	<25	<25
Dieldrin	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<2500	<25	<25	<25	<25	<25	<25	<25	<25
Estradiol	**1.5**	<1	**2.9**	**1.5**	<1	**2.9**	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Estrone	**35**	<1	**70**	**0.8**	<1	**1.6**	**31**	**35.5**	<1	**71**	<1	<1	<1	<1	**50**	**12**	**39**	**2.5**	<1	**4.9**	**7**	**1.8**	<1
Ethinyl Estradiol -17 alpha	<1	<1	<1	**31.5**	<5	**63**	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Fluoxetine	<1	<1	<1	**52.6**	<1	**104**	**14**	**17**	<1	**34**	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Gemfibrozil	NA	NA	NA	**9**	<1	**18**	**5.5**	**8.5**	<1	**17**	**3.8**	**0.9**	NA	**1.7**	**1020**	**26**	**11**	**5.1**	<1	**10**	<1	**43**	<1
Ibuprofen	NA	<1	NA	**14.6**	<1	**26**	<1	<1	<1	<1	**2.9**	**2.4**	<1	**3.7**	**7000**	**6**	**2.8**	**3.1**	<1	**6.1**	**2.7**	**8140**	**21**
Iopromide	<5	<5	<5	<5	<5	<5	**11**	**17.5**	<5	**35**	**13**	**8**	<5	**16**	<500	<5	<5	<5	<5	<5	<5	<5	<5
Methyl Parathion	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<2500	<25	<25	<25	<25	<25	<25	<25	<25
Phenol	<100	<100	<100	<100	<100	<100	<100	**126**	<100	**252**	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	**258**	**955**
Progesterone	<1	<1	<1	<1	<1	<1	<1	**0.6**	<1	**1.2**	<1	<1	<1	<1	<100	<1	<1	<1	<1	<1	<1	<1	<1
Sulfamethoxazole	**78.5**	<1	**156**	**283**	<1	**565**	**62**	**155**	<1	**310**	**46**	**210**	<1	**420**	**854**	**363**	**28**	**22.8**	<1	**45**	**76**	**768**	**3.5**
Tris (1,3-dichloro-2-propyl) phosphate	**138.5**	<25	**277**	**212**	NA*	**324**	**186**	**176.5**	<25	**353**	**148**	**169.5**	NA*	**258**	<2500	**94**	**121**	**108.4**	<25	**214**	<25	<25	<25
Testosterone	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	**75**	<1	1	<1	<1	<1	<1	**1**	<1
Triclosan	**17.5**	<5	**35**	**71**	<5	**142**	**32**	**23**	<5	**46**	**42**	**19**	<1	**38**	<500	<5	<5	<5	<5	<5	<5	<50	<50
Triclosan	**42**	<50	**84**	**52.5**	<50	**105**	<50	**34.5**	<50	**69**	<50	<50	<50	<50	**5500**	<50	<50	**46.1**	<50	**91**	<50	<5	<5
Trimethoprim	**0.6**	<1	**1.2**	**22.2**	**1.3**	**43**	**1**	**0.8**	<1	**1.5**	<1	<1	<1	<1	**36**	<1	<1	<1	<1	<1	<1	**32**	<1
Triphenylphosphate	<25	<25	<25	<25	<25	<25	**52**	**59.5**	<25	**119**	**44**	**65.5**	<25	**131**	<2500	**57**	**72**	**50.1**	<25	**99**	<25	<25	<25
Tris (2-butoxyethyl) phosphate (TBEP)	<100	<100	<100	**52.5**	<100	**105**	<100	<100	<100	<100	**140**	**196**	<100	**392**	<10000	**148**	**935**	**97.2**	<100	**192**	**352**	<100	**108**
Tris (2-chloroethyl) phosphate (TCEP)	**71.5**	<25	**143**	**99.5**	<25	**199**	**137**	**151.5**	<25	**303**	**64**	**84.5**	<25	**169**	<2500	**93**	**118**	**95.2**	<25	**188**	<25	<10	<10

Notes:
1. Microconstituents in RO influent were calculated based on their concentrations in RO effluent and RO brine and their flow rates.
2. RO brine is rejected RO influent with highly concentrated salts.
3. RO effluent is the effluent water after reverse osmosis treatment.
NA. not available due to low sample recovery.
NA*. not available due to potential contamination.

3.3. Toxicity Testing

The survival and growth of *P. promelas* and survival and reproduction of *C. dubia* were used to evaluate the toxicity of various effluents in the AWT facility and canal water. Five toxicity tests were conducted on 10/29/2007, 11/26/2007, 1/14/2008, 1/31/2008, and 2/21/2008, respectively.

The survival results on 10/29/2007 indicated that RO effluent could result in 100% mortality of the test organism, *C. dubia*. Because microconstituents in the RO effluent were all non-detectable, the observed toxic effects were likely caused by other compounds added or generated in the RO effluents. After ruling out the potential effects from RO stabilization chemicals or other water quality parameters (dissolved oxygen, pH, trace minerals), a further evaluation of the RO system indicated that ammonia, chloramine, and antiscalant used for maintaining the RO system might contribute to the observed toxicity. Therefore, tests in which the RO effluent samples were quenched with sodium thiosulfate, thus reducing the combined chlorine to below detection, were performed for the second round of testing on 11/26/2007. The dechlorination (quenching) of chloramine reduced and delayed toxicity but did not abolish it. To further diagnos the cause of toxicity, all additions (ammonia, chloramine and antiscalant) were stopped prior to water being sampled on 1/14/2008. The results showed that RO effluent did not produce any significant toxicity and the survival of P. promelas and *C. dubia* significantly increased. The fourth and fifth tests were used to further evaluate if the previously observed toxicity were caused by chloramine or antiscalant. For the fourth round of testing on 1/31/2008, only chloramine was added to the system and no antiscalant were used. For the fifth round of testing on 2/21/2008, only antiscalant was added to the system and no chloramine was used. Overall, these results demonstrate the toxicity observed with RO effluents is due to the presence of the compounds added to improve process performance. Chlorinated compounds (chloramines) are the most likely causes of toxicity.

Detailed results on toxicity of MBR effluent, UF effluent, and RO effluent are shown in Figures 3-10 - 3-17 and discussed in the following sections.

3.3.1. Toxicity of MBR and UF effluent

The survival of *P. promelas* and *C. dubia* in MBR or UF effluent are shown in Figures 3-10 and 3-11. The growth of *P. promelas* and reproduction of *C. dubia* in MBR or UF effluent are shown in Figures 3-12 and 3-13.

No significant survival differences in MBR and UF effluent above control (de-ionized water) were observed for *P. promelas* (Figure 3-10) and *C. dubia* (Figure 3-11) on 10/29/07, except that the survivability of *C. dubia* was low in 100% MBR effluent. No significant growth differences in MBR and UF effluent above control (de-ionized water) were observed for *P. promelas* (Figure 3-12). Similarly, no significant reproduction differences in MBR or UF effluent above control (de-ionized water) were observed for *C. dubia* (Figure 3-13). These results suggest that MBR effluent and UF effluent did not have significant toxic effects on the survival and growth of *P. promelas* and survival and reproduction of *C. dubia*. Notice that the chloramines and antiscalant are added *after* the MBR/UF membranes and thus there are no chloramines in the MBR/UF effluent for any of the tests performed here.

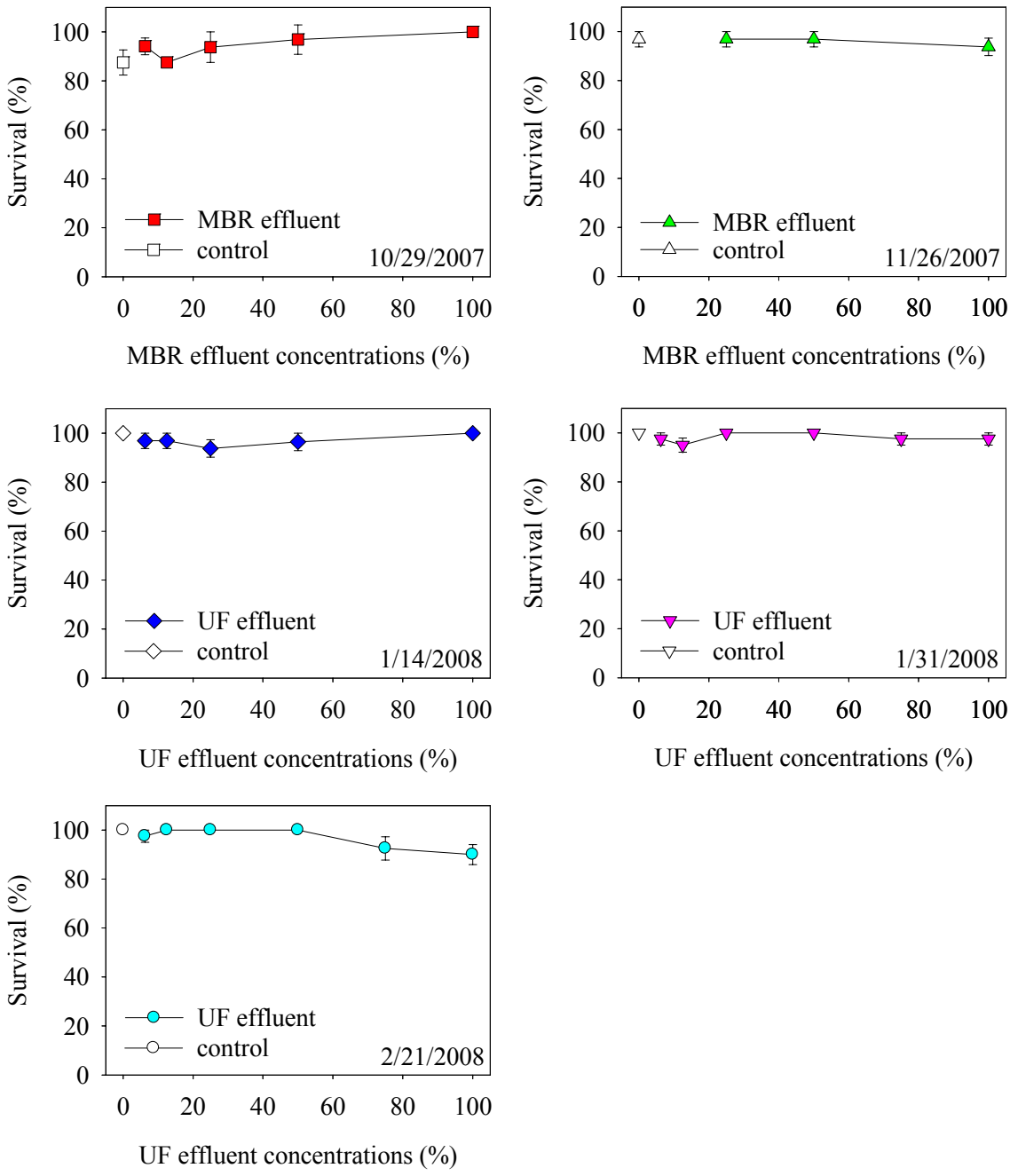


Figure 3-10. Survival of *P. promelas* in MBR effluent and UF effluent

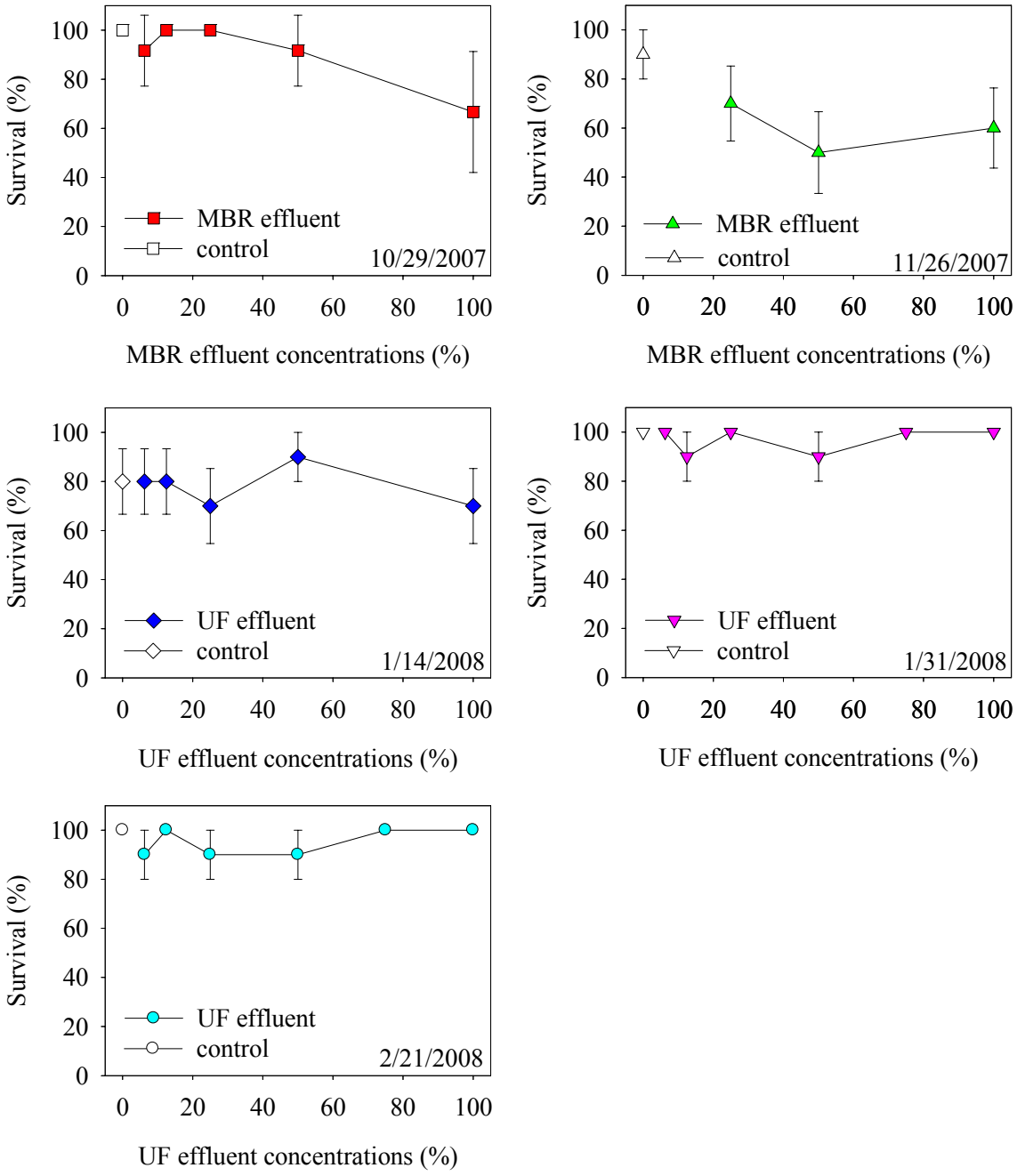


Figure 3-11. Survival of *C. dubia* in MBR effluent and UF effluent

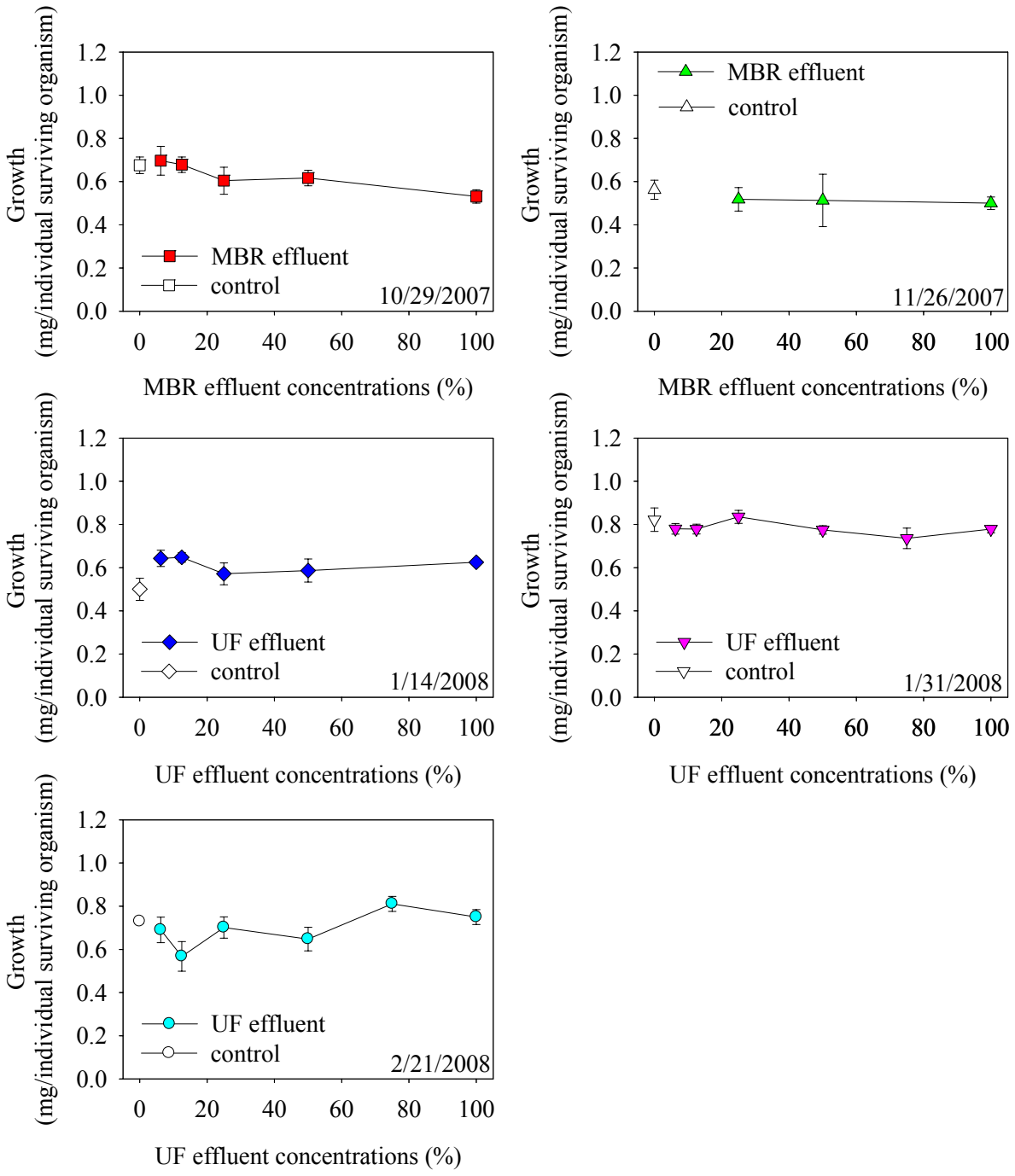


Figure 3-12. Growth of *P. promelas* in MBR effluent and UF effluent

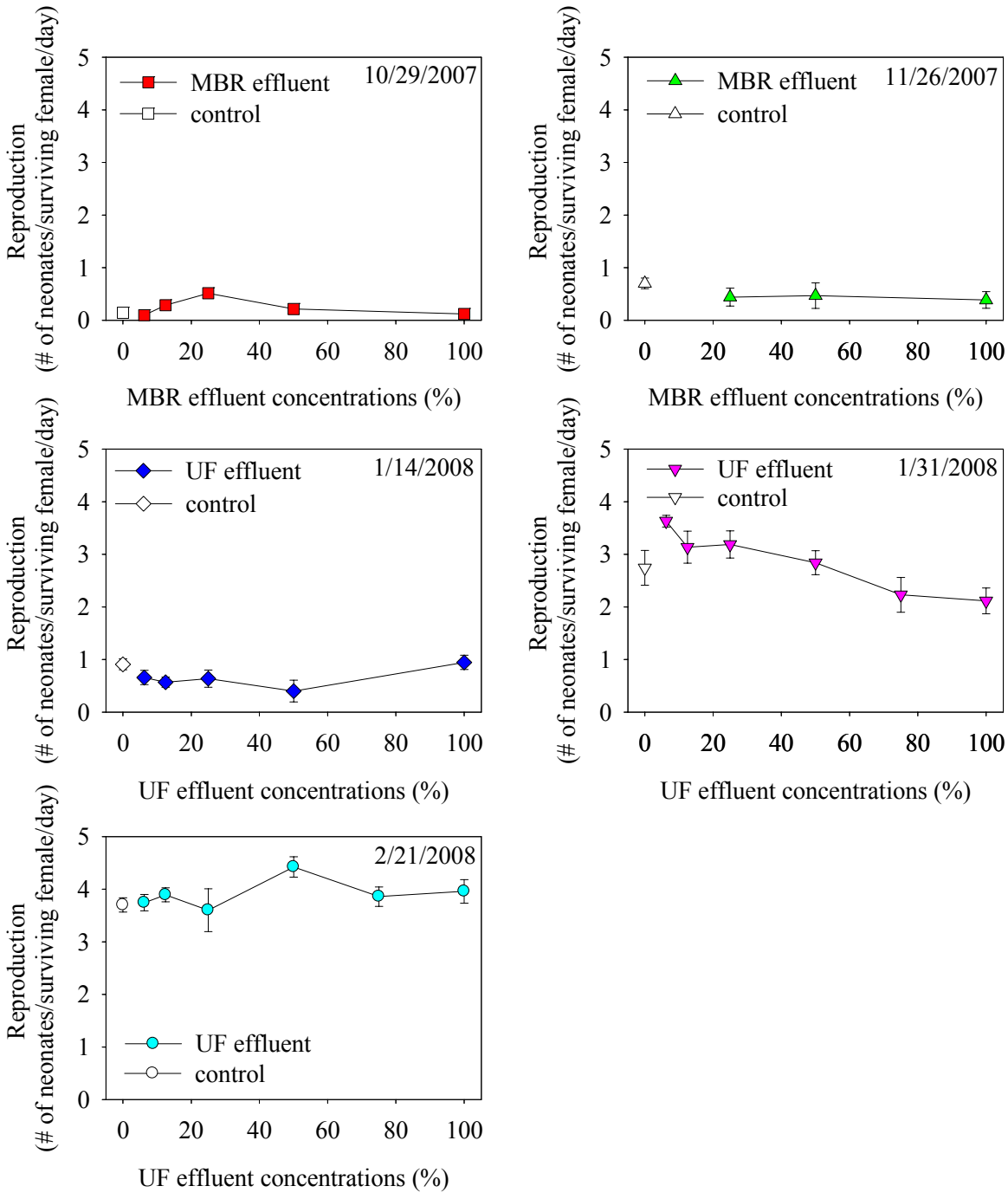


Figure 3-13. Reproduction of *C. dubia* in MBR effluent and UF effluent

3.3.2. Toxicity of RO effluent and canal water

The survival of *P. promelas* and *C. dubia* in RO effluent are shown in Figures 3-14 and 3-15. The growth of *P. promelas* and reproduction of *C. dubia* in RO effluent are shown in Figures 3-16 and 3-17.

The survivability of *P. promelas* and *C. dubia* in RO effluent were low on 10/29/2007 with 100% mortality of *C. dubia* and some mortality of *P. promelas* potentially caused by chloramine in RO effluent. Therefore, RO effluent samples were quenched with sodium thiosulfate, reducing the combined chlorine to below detection for the second round of testing on 11/26/2007. The survivability of *P. promelas* and *C. dubia* in RO effluents significantly increased after quenching (dechlorination). No significant survival differences above control were observed in *P. promelas* after dechlorination, which suggests that toxicity was completely removed after dechlorination. Conversely, the survivability of *C. dubia* in less diluted (> 25%) RO effluent, which contained antiscalant and quenched chloramine, was still low after dechlorination. Further experiments on 1/14/2008 without chloramine and antiscalant showed no survival differences between RO effluent and control and significant increase in reproduction of *C. dubia*. No significant survival differences above control were observed in *P. promelas.* The experiment on 1/31/2008 with only quenched chloramine showed significant increase of *C. dubia* survival in RO effluent compared with the condition with unquenched chloramine, but toxicity was only partially reduced after quenching, which was probably caused by a trace amount of ammonia in the water resulting from dechlorination of samples. No significant survival differences above control were observed in *P. promelas.* The final batch of experiments on 2/21/2008 with only antiscalant indicated that there was no significant survival and growth differences of *P. promelas* in RO effluent and control (de-ionized water) and there was no significant survival and reproduction differences of *C. dubia* in RO effluent and control (de-ionized water). These results suggested that antiscalant did not have toxicity effects on *C. dubia*, and the observed toxicity was likely caused by chloramine.

Surface (canal) water was also tested to evaluate the background toxicity in the canal. No significant differences of the survival and growth of *P. promelas* and survival and reproduction of *C. dubia* were observed between canal water and control, suggesting that canal water did not pose any toxicity to the survival and growth of *P. promelas* and survival and reproduction of *C. dubia*.

The fact that *P. promelas* and *C. dubia* had no survival differences in MBR effluent and UF effluents compared to controls and the observed toxicity to *C. dubia* from RO effluents were delayed and removed after chloramine were stopped or quenched suggest that microconstituents did not contribute to the toxicity of AWT facilities. Instead, these results suggest that chloramines or ammonia in these systems may contribute to the toxicity to *C. dubia* and should be removed by break point dechlorination, advanced oxidation, or other quenching methods. To facilitate surface water augmentation, the toxicity of chloramine for maintaining AWT facilities deserves further investigation.

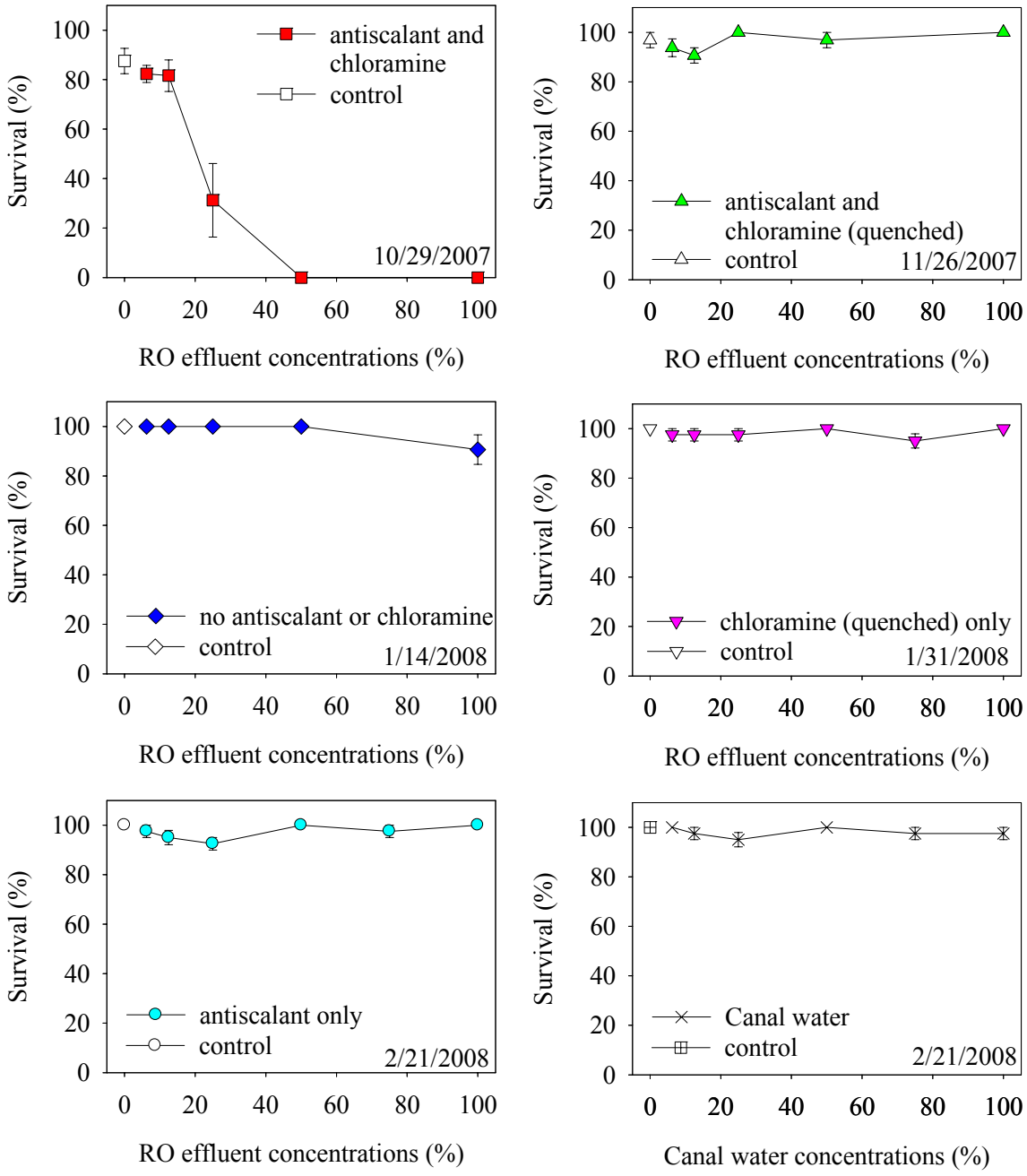


Figure 3-14. Survival of *P. promelas* in RO effluent and canal water

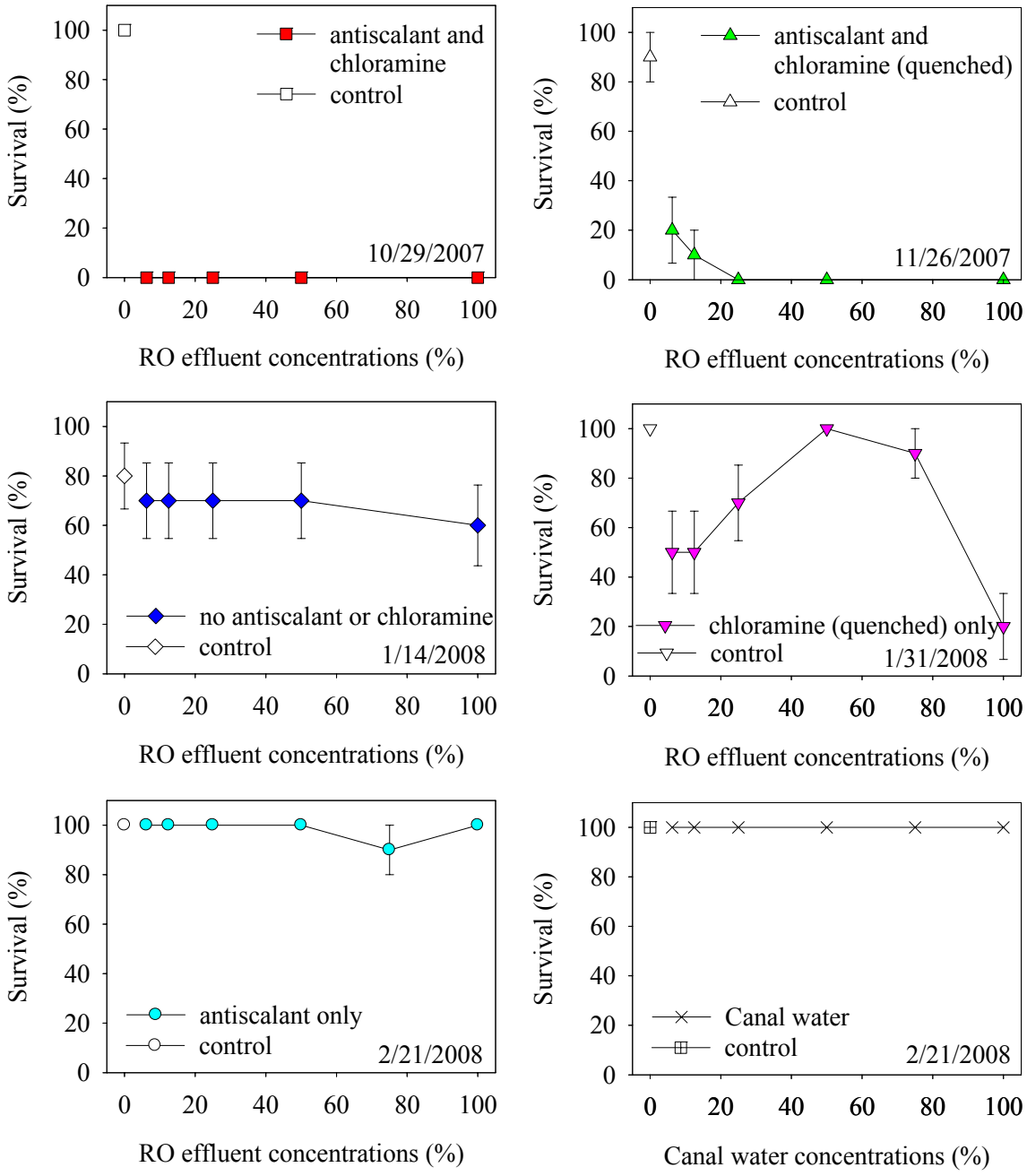


Figure 3-15. Survival of *C. dubia* in RO effluent and canal water

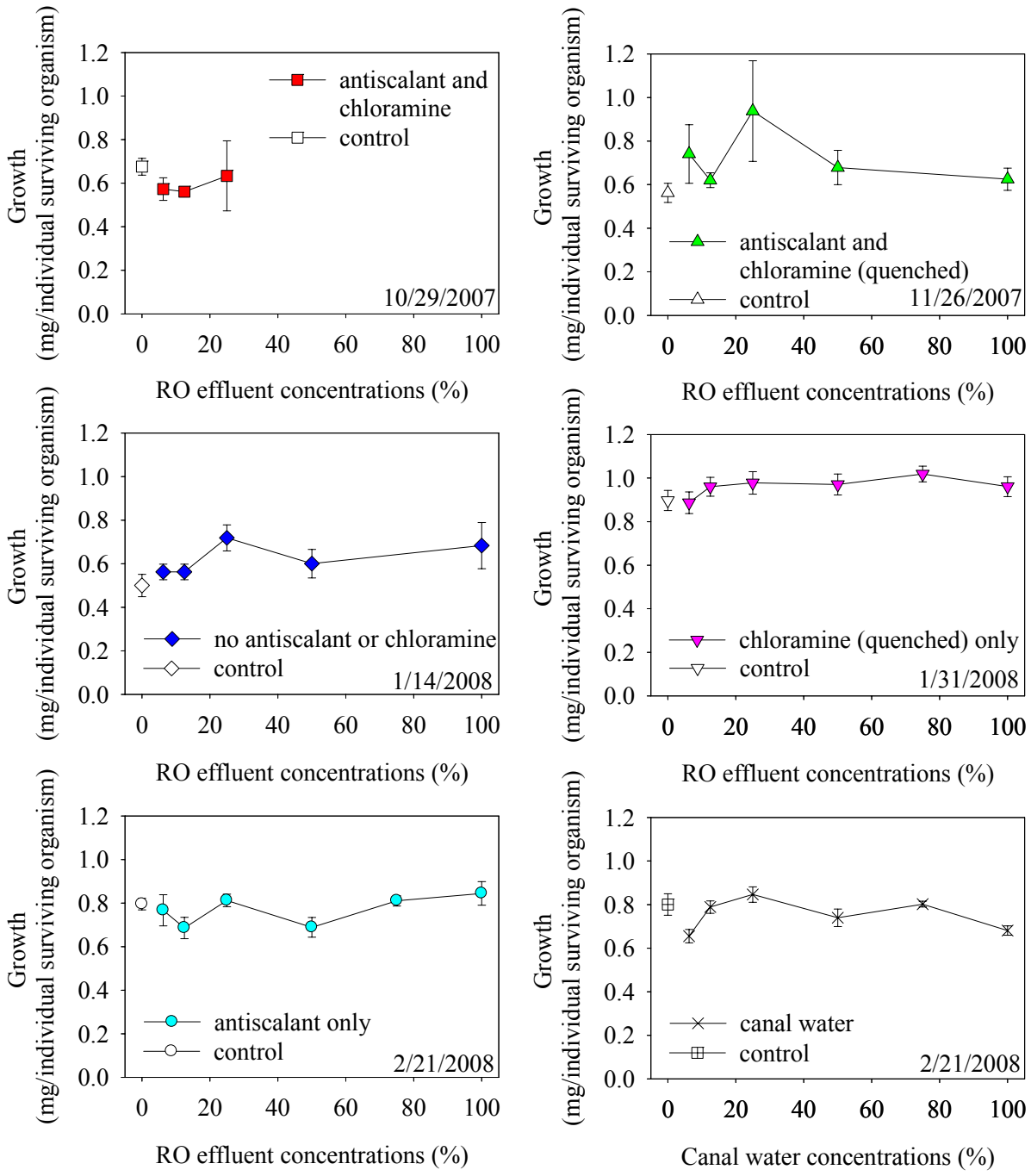


Figure 3-16. Growth of *P. promelas* in RO effluent and canal water

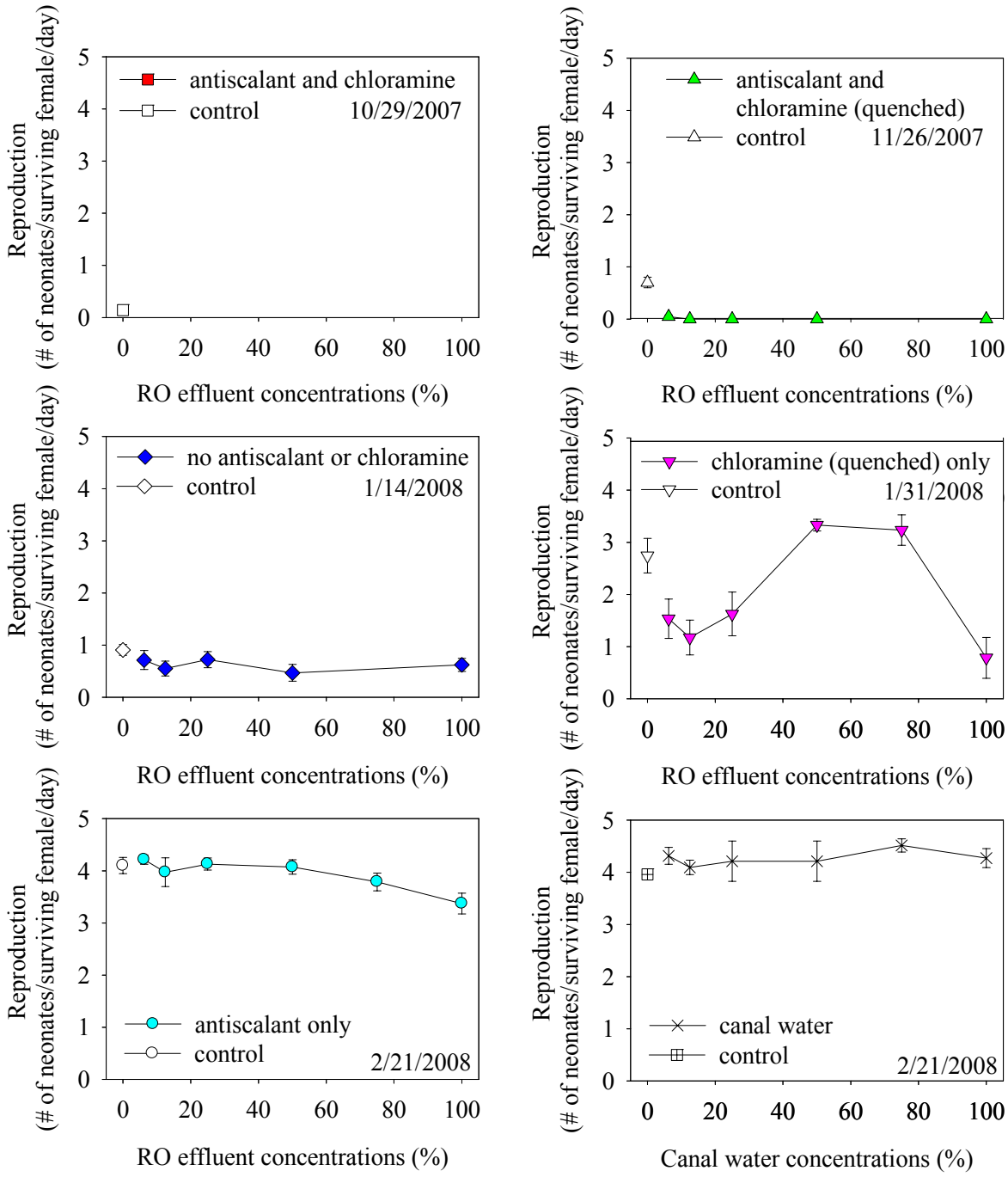


Figure 3-17. Reproduction of *C. dubia* in RO effluent and canal water

3.4. E-Screen Bioassay

The results of E-Screen bioassay are shown in Figure 3-18. Although estradiol equivalents were detected in secondary effluent, DNF effluent, MBR effluents, and UF effluents, estradiol equivalents in all RO effluents were below detection limits. The results of E-Screen bioassay indicate that RO effluent did not produce a significant response in MCF-7 cells.

3.5. Yeast Estrogen Screen Assay

Similar to that of the E-screen, the response of the yeast cells to the sample extracts was compared with that of a standard curve in YES assay to determine the estradiol equivalents of effluent samples. The results of the YES assays are shown in Figure 3-19. Although estradiol equivalents were detected in secondary effluent and DNF effluent, estradiol equivalents in MBR effluents, UF effluents, and RO effluents were below detection limits. The results of YES bioassay indicated that MBR effluent and RO effluent didn't possess endocrine disrupting potential.

3.6. Fathead Minnow Vitellogenin and Steroid Assays

The results of the fathead minnow vitellogenin assays of MBR/RO system are shown in Figure 3-20. The positive EE2 and negative controls worked as predicted for the MBR/ RO system. None of the effluents tested in MBR/RO system showed an increase of plasma Vtg in male fish, indicating that they are not exposed to estrogenic components at the required concentrations for this effect.

The results of the fathead minnow vitellogenin assays of UF/RO system are also shown in Figure 3-20. Effluents from DNF effluent and RO effluent show estrogenic effects by increasing plasma vitellogenin to 6 and 5 mg/L respectively, both are considered to be very low concentrations of plasma vitellogenin. The 5 ng/L EE2 positive control was less potent than expected, and this was due to lower actual concentrations in the control test water - about 2 ng/L rather than designed 5 ng/L. However, the EE2 positive control did produce a positive result, showing that the assay worked. Please note the limit of detection of the assay is 0.5 mg/L and negative control values in male fish are normally below 1 mg/L. Male fish that have a positive response to an estrogenic substance are usually above 10 mg/L, thus none of these fish exhibit a true positive response.

The results of fathead minnow steroid assays are shown in Figure 3-21. Plasma samples obtained from mail fathead minnows were analyzed for testosterone by ELISA following extraction. Testosterone concentrations in all treatments were similar to those in the negative control group. There was no significant difference in plasma testosterone for any of the treatments compared to negative controls. The mean values of testosterone in UF effluent and canal water as well as EE2 (5 ng/L ethinyl estradiol) tended to be higher than controls, though this was driven by 1 or 2 individual fish with very high levels of testosterone, which caused high variability as well as increased average testosterone levels. The reason for the high levels of testosterone in these fish is unclear, but may be related to behavioral dominance (alpha males) or other causes. There is no correlation of high testosterone values with vitellogenin induction, suggesting that the testosterone values are not due to estrogenic effects of the effluents. All of these results suggest that RO effluents were not estrogenic.

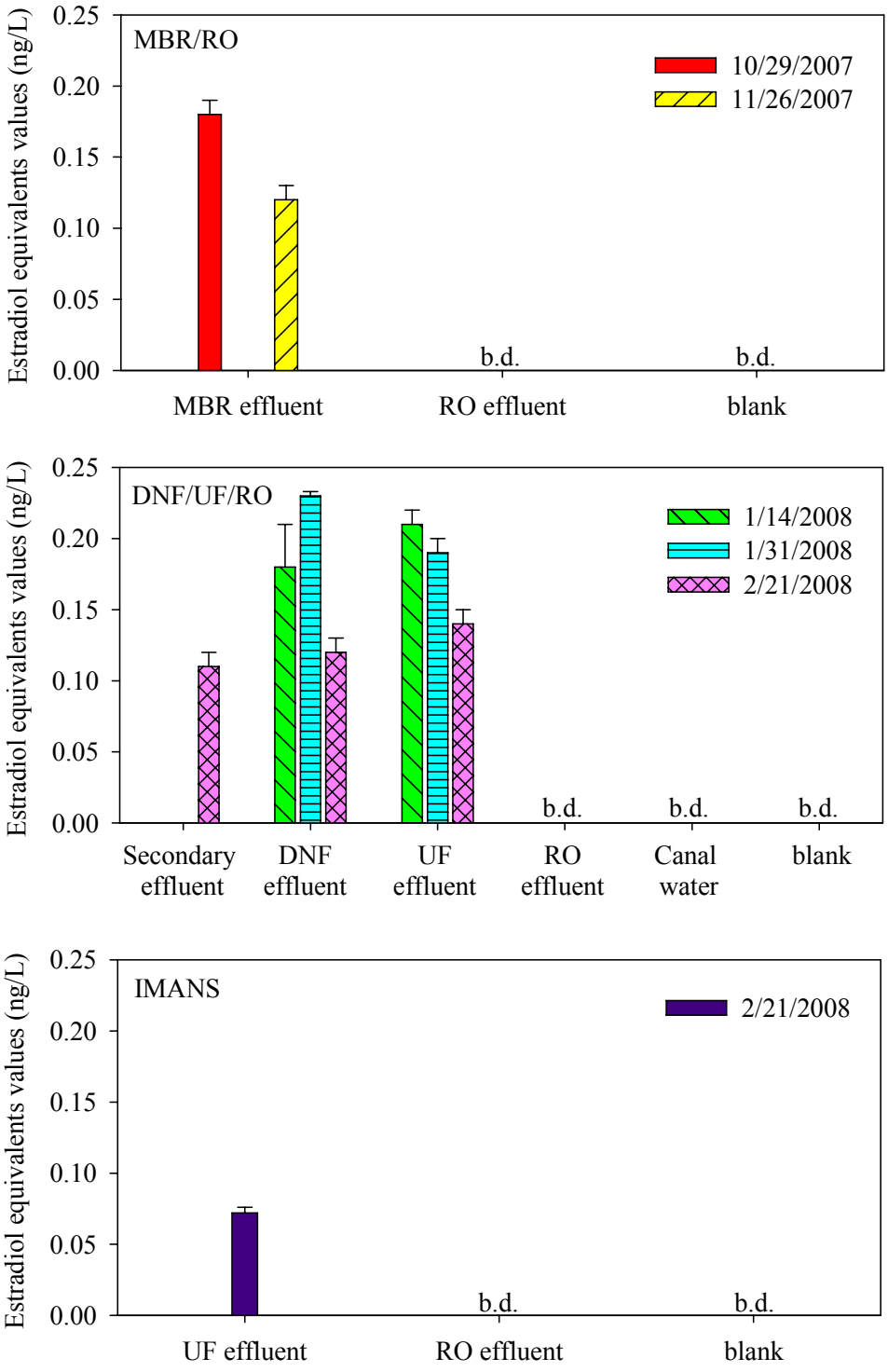


Figure 3-18. Results of E-Screen bioassay
b.d.: below detection limits (estradiol equivalent < 0.03 mg/L)

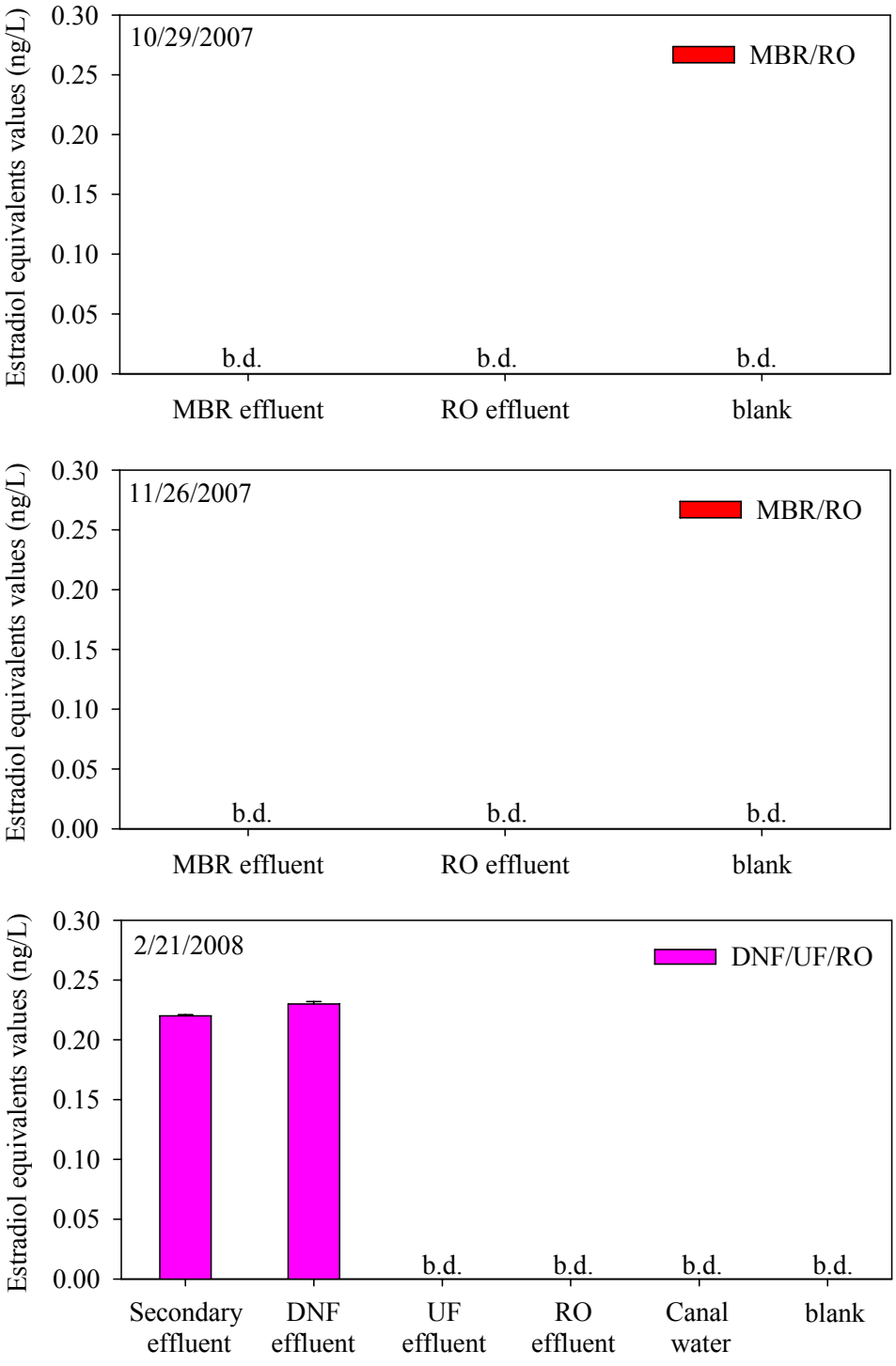


Figure 3-19. Results of YES assay
b.d.: below detection limits (estradiol equivalent < 0.20 mg/L)

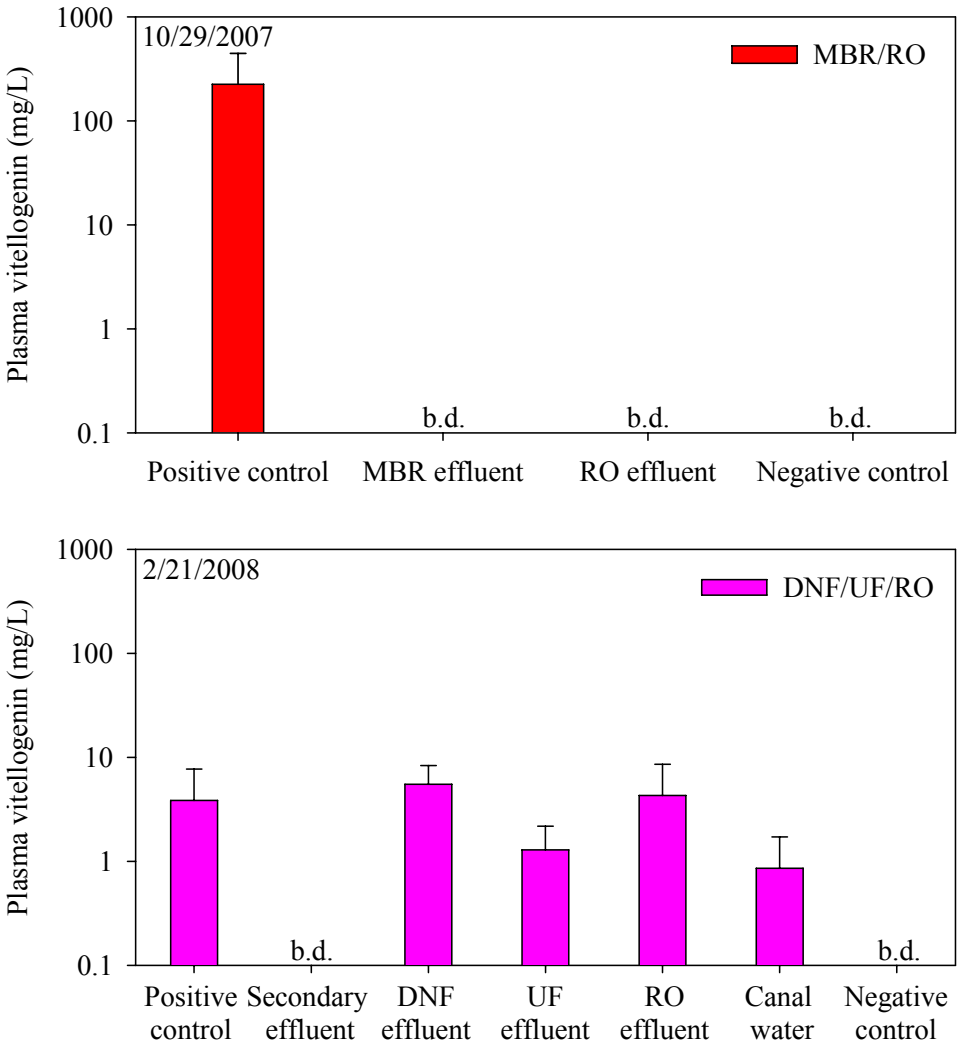


Figure 3-20. Results of fathead minnow vitellogenin assay
b.d.: below detection limits (plasma vitellogenin < 0.5 mg/L)

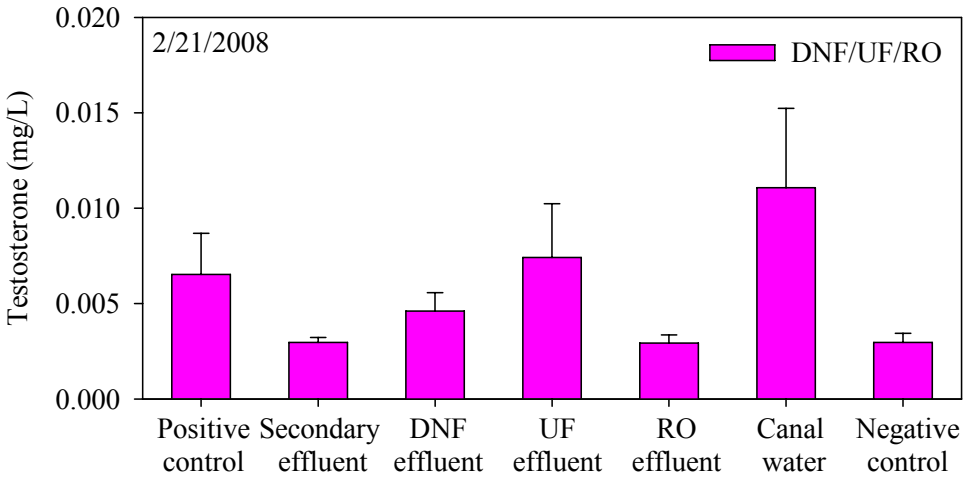


Figure 3-21. Results of steroid assay.

3.7. Recharge Modeling

The main objective of the modeling work was to estimate the fate and transport of three microconstituents and one conservative tracer from its hypothetical source (point of reclaimed water discharge), through a canal network, and through the surficial aquifer system. In doing so, the project team examined open channel and groundwater hydraulics, along with chemical transport in the surface water and groundwater. The three microconstituente were sulfamethoxazole, phenol, and triclosan.

3.7.1. Hydrodynamic model

The water elevation and discharge rate predicted by the model in the Holloway canal at the WWTP effluent location is shown in Figure 3-22. In order to show the effect of the reclaimed water discharge, the case of no discharge from the WWTP effluent is also included. For the purpose of this model, a reclaimed water discharge rate of 5 ft^3/s is assumed. In the wetter months (May to October) water levels at that site are commonly between 3.5 and 4.5 ft. The upper limit is controlled by downstream pumps that release water if the upstream water levels are higher than 4.5 ft. Canals in MIKE 11 receive runoff from overland flow and groundwater drainage and lose water due to infiltration. Evaporation loses directly from the river network are only considered by the model in the primary canals (North New River and C-12). Infiltration losses are evident in the drier months (November to April) when the water levels are around 3 and 3.5 ft. Note that in the case of no discharge from the WWTP, the water levels for the dry season are approximately 0.25 ft lower.

The flow rates in the Holloway canal at the WWTP effluent location also show a seasonal dependence, as seen in Figure 3-22. During the wet season the direction of the flow predicted by the model is positive, which means a flow from north to south. However, during the drier months the magnitude of the flow is lower and the direction may change more frequently.

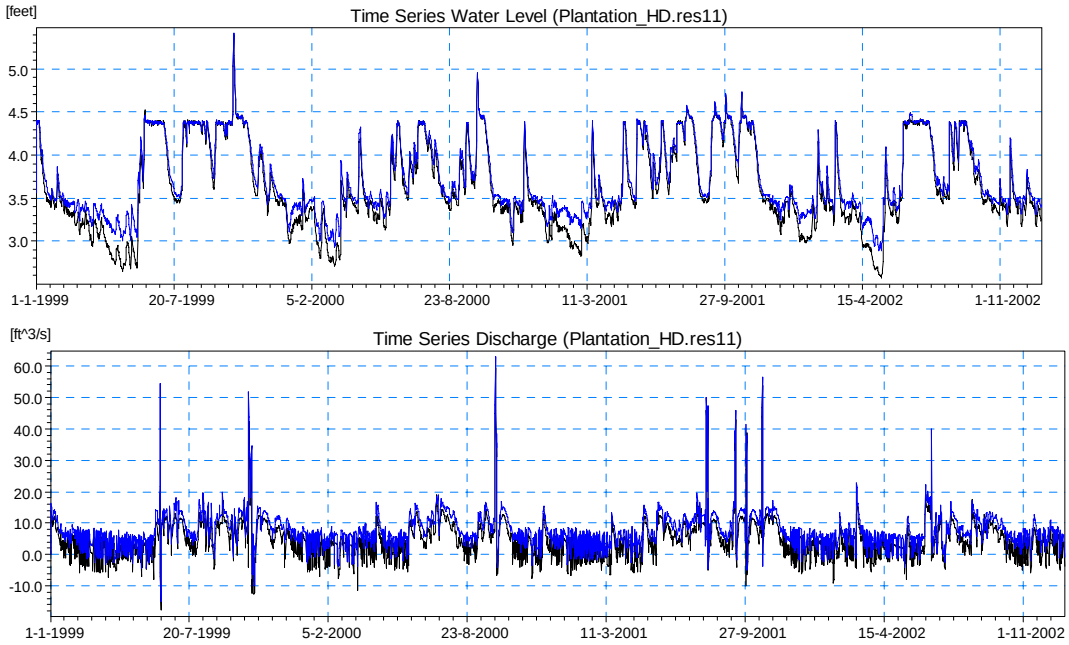


Figure 3-22.Water levels and discharge rate in the Holloway canal at WWTP effluent location as predicted by the model. Blue and black lines represent the cases with an effluent discharge of 5 ft^3/s and without it, respectively.

Potable water supply wells are extracting water mostly from the groundwater (computational) layers 3, 4 and 5 of the model. The spatial distribution of the head in the upper layer (layer 3) is shown in Figure 3-23. Notice that the head decreases in general from west to east. However, the extraction at some wellfields causes a head drawdown that modifies that regional pattern. The groundwater flow is driven by the head differences from high to low values.

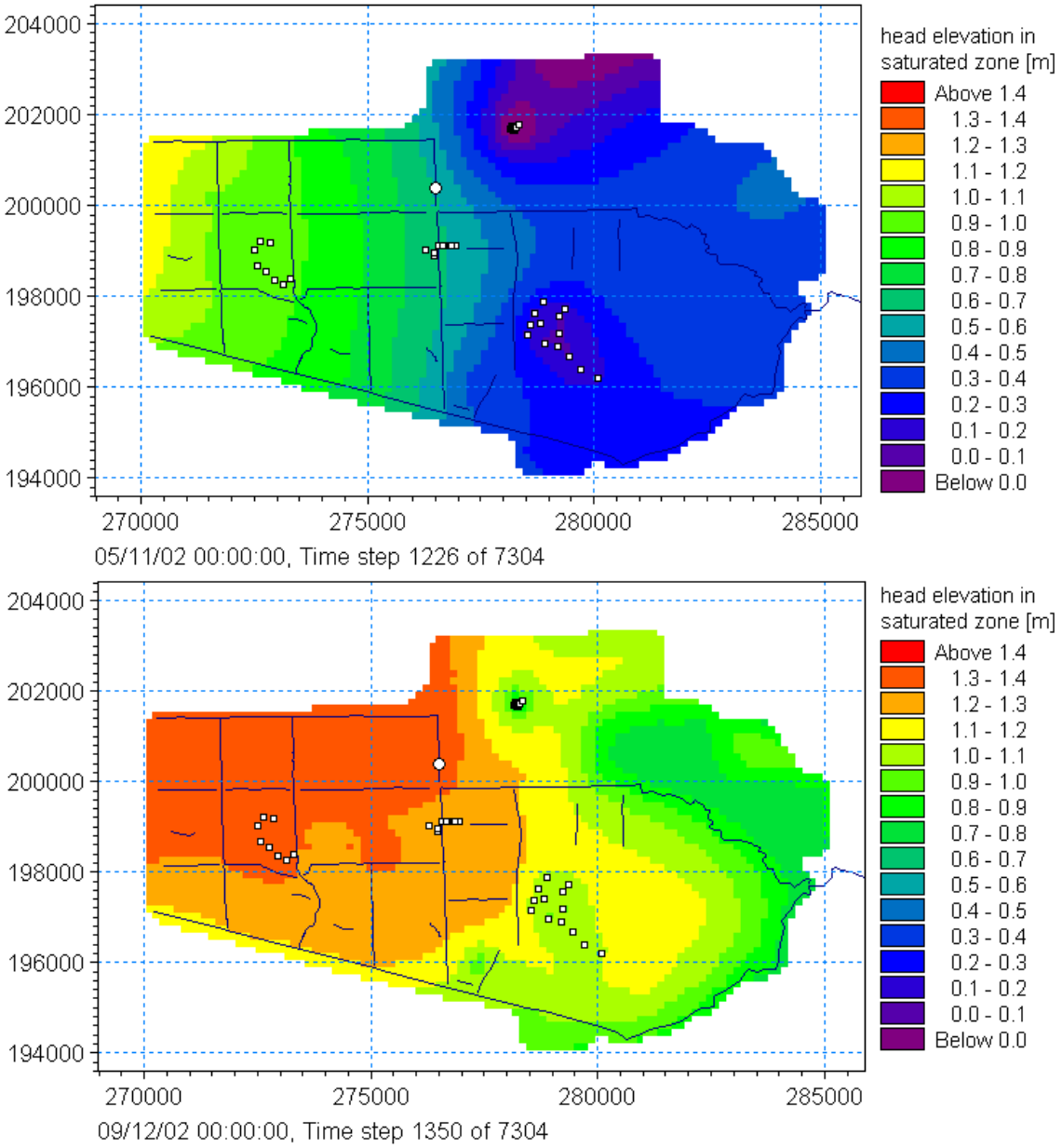


Figure 3-23.Head elevation in groundwater (computational) layer 3 at the end of the dry and wet seasons of year 2002 in m NGVD29. The white circle represents the WWTP effluent location and the small white squares the place of the extraction wells. Geographical coordinates are also in m.

A sketch of the average annual water budget for the four years considered (1999-2002) is presented in Figure 3-24. The figure shows that the well extraction from Layer 3 is the largest, followed by layer 4.

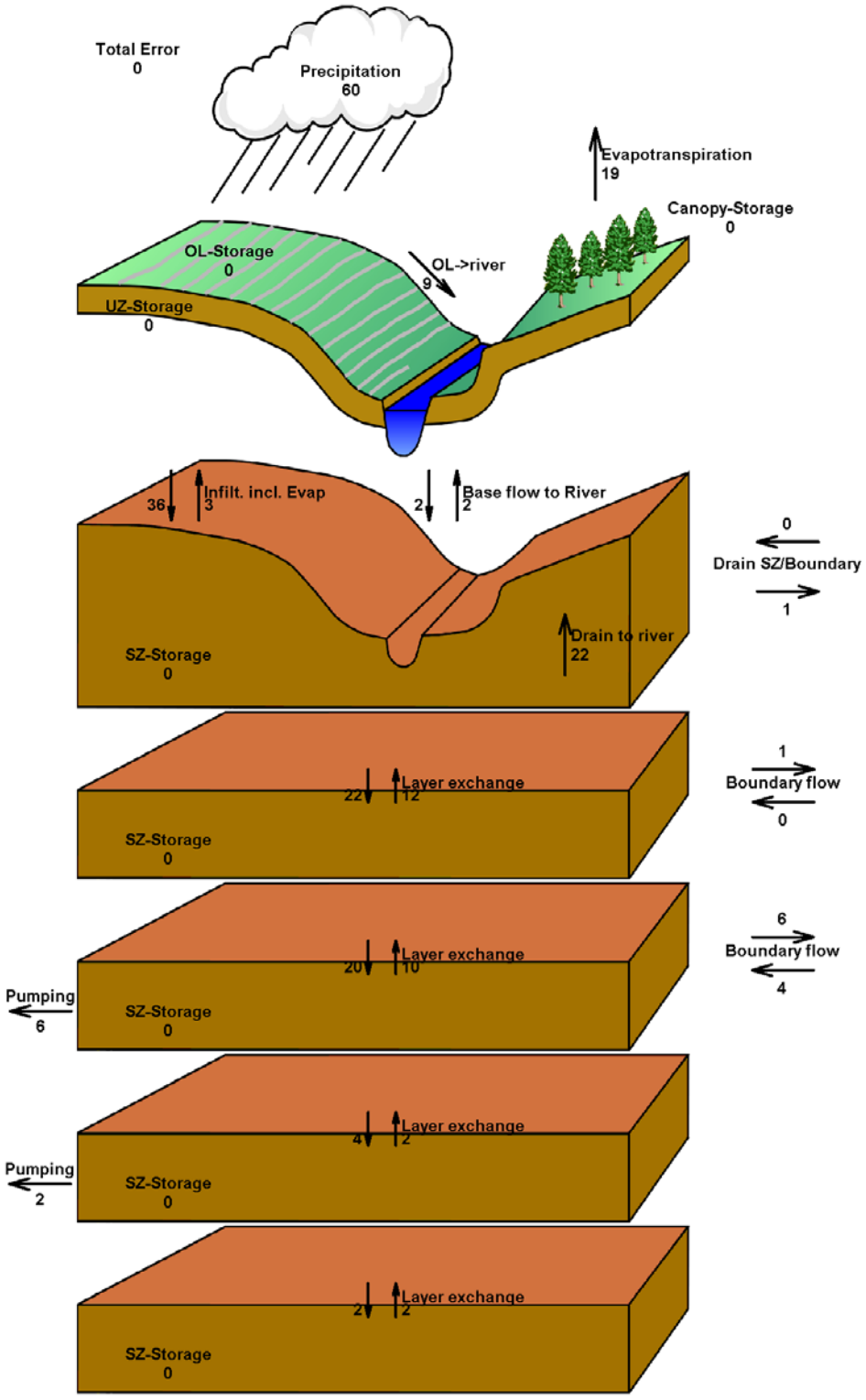


Figure 3--24.Annual average water budget for the whole hydrodynamic MIKE SHE model domain area. Numbers are depths (volume per unit of horizontal area) in inches/yr. OL stands for overland flow, UZ for unsaturated zone and SZ for saturated zone.

The model was run for a two-year period (2001 - 2002). This period falls within the Broward model calibration period (1999-2002) and it represents a period of average rainfall conditions.

Some surface and groundwater simulated results with the observed data are shown below. In general the groundwater results follow the observed data closely (Figure 3-25). The surface water results are very sensitive to the structure operations (Figure 3-26), which tend to differ in practice from the written protocols. As shown below, the S-33 gates in the model are operating to maintain the control elevation for the C-12 basin (3.5 feet).

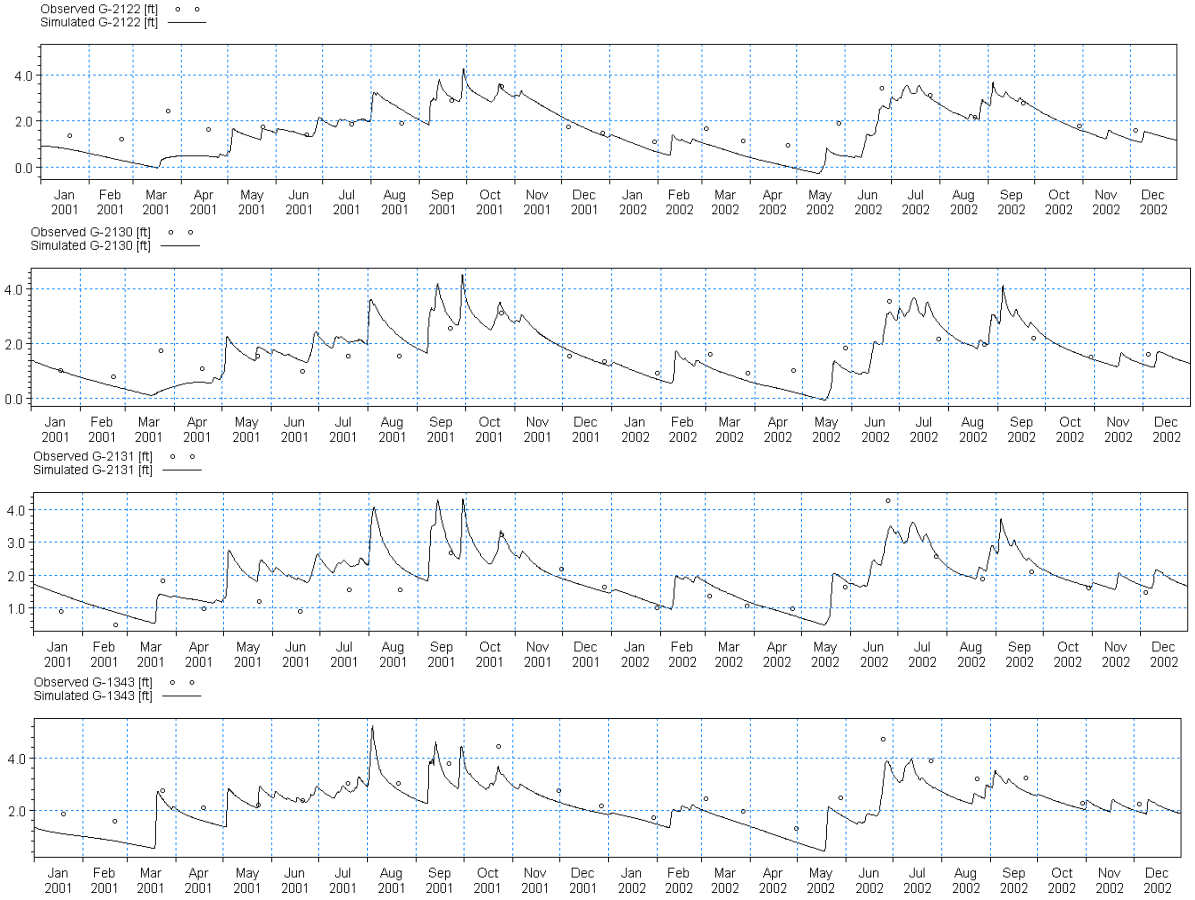


Figure 3-25. Groundwater plots

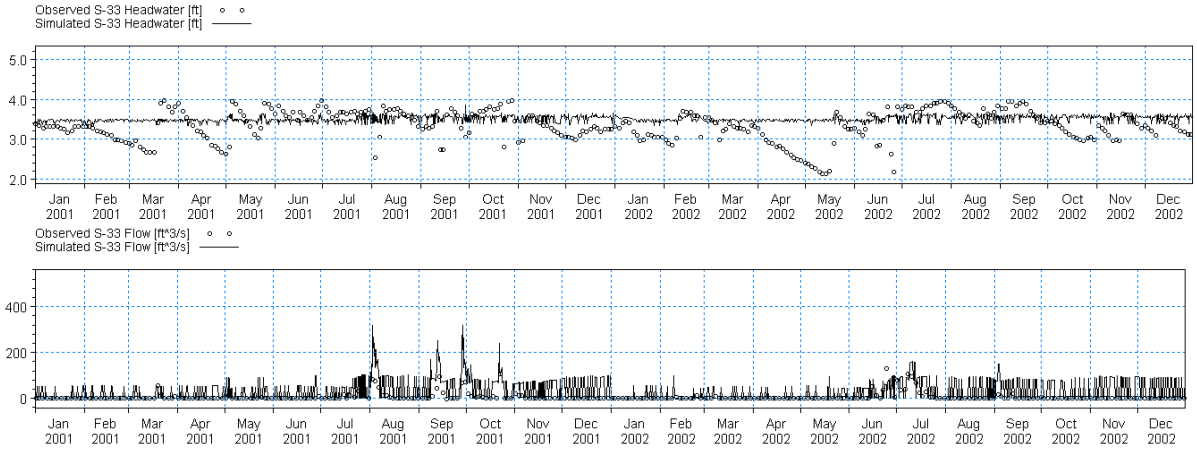


Figure 3-26. Surface water plots

3.7.2. Water quality model

The water quality section is divided into two subsections; the first shows the transport of suspended sediment and the second shows the transport of the conservative tracer and the three microconstituents considered.

3.7.2.1. Sediment transport

The results for sediment transport in canals at the hypothetical reclaimed water discharge location are shown in Figure 3-27. In general, the suspended particles concentration fluctuates around 1 mg/l, which corresponds to the equilibrium concentration when water speed is approximately 0.4 cm/s (0.013 ft/s). During the wet season, the higher water velocities cause higher resuspension and therefore higher concentration of suspended particles. In heavy rainfall events, the concentration may reach 5 mg/l. During the dry season the water velocities in the canal network are lower and so are the resuspension and the suspended particles concentration.

The graph for the suspended particles concentration looks similar every time the water movement data is recycled (4 years), except by the effect of the initial conditions assumed at the beginning. However, the mass of the sediment layer at the hypothetical reclaimed water discharge location increases initially and then decreases. This may indicate that the predicted changes in the sediment layer thickness continue after 20 years. A view of this variable in the whole canal network at the end of the simulation is shown in Figure 3-28. The locations of larger mass of sediment roughly correspond to the locations of higher flow rates shown in the model. However, since the resuspension rate depends directly on the water velocity and not on the volumetric flow rate, the final mass of sediment also depends on the cross-sectional area of the canals.

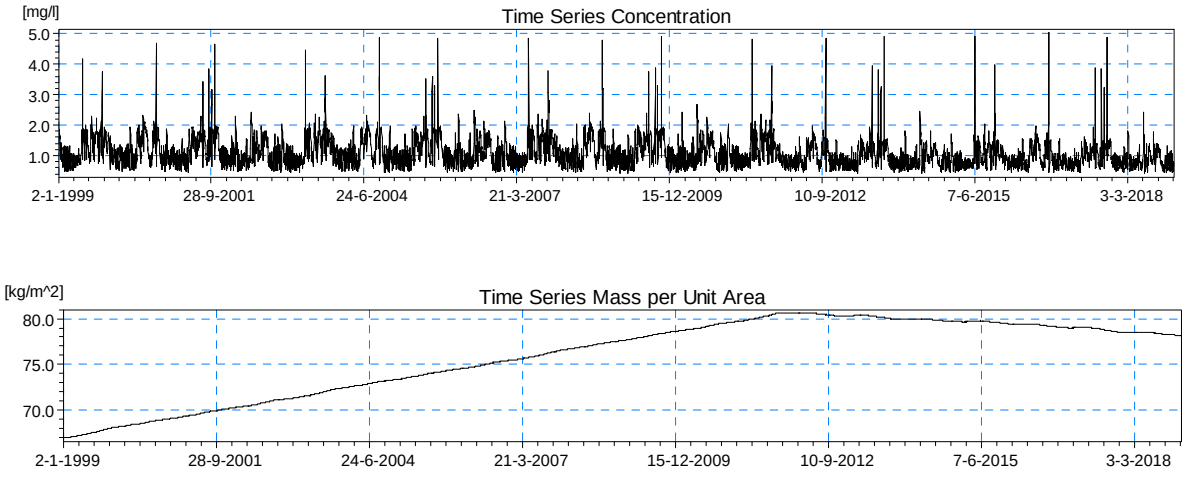


Figure 3.27.Simulated concentration of suspended particles and the mass of sediment layer in the Holloway canal at the WWTP for the whole simulation period (20 years).

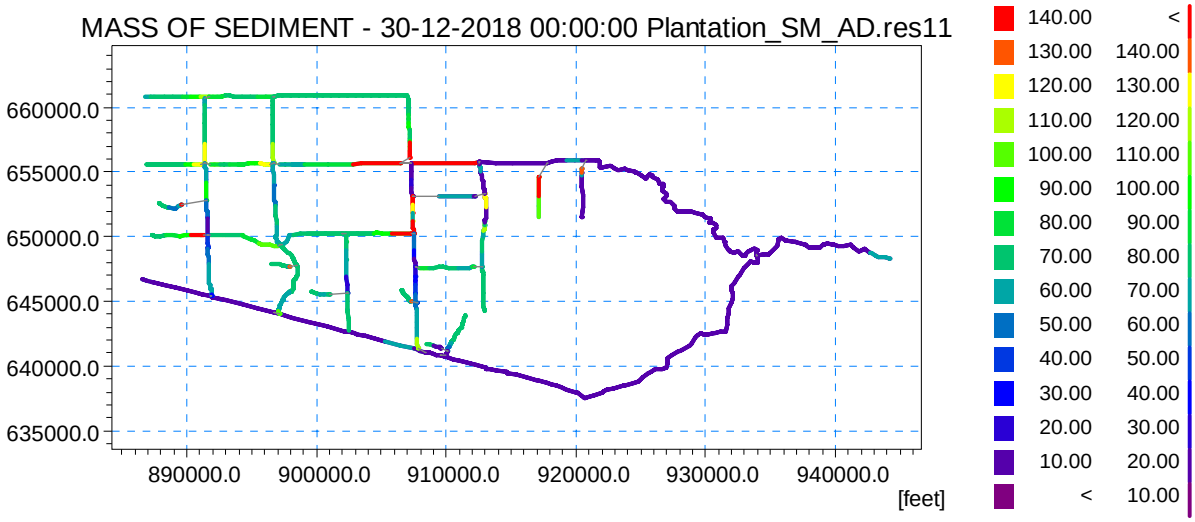


Figure 3-28.Simulated mass of sediment layer (kg/m^2) in the canal network at the end of the simulation period.

3.7.2.2. Microconstituent transport

Figure 3-29 shows the concentrations for the three microconstituents and the conservative tracer in the Holloway canal at the hypothetical reclaimed water discharge location for the period of 1999-2002. For sulfamethoxazole (SM), phenol (PH), and conservative tracer (CT), the concentration stabilizes after a short period. However, for Triclosan (TS) the concentration in the water column takes several years to reach asymptotic values from the zero-concentration initial condition as shown in Figure 3-30. The adsorption coefficient of TS is more than 10 times higher than the assumed adsorption coefficient in the other microconstituents considered, which makes the stabilization of the concentration a slower process.

The dissolved concentration divided by the concentration at the WWTP effluent gives a relative concentration, which serves to compare the effect of different processes (adsorption, biodegradation, photolysis and evaporation) on the microconstituent concentrations. Moreover, the results expressed as relative concentration are independent on the effluent concentration (due to the linearity of the processes involved) and they can be extrapolated to other assumed effluent concentrations.

The relative SM, PH, TS, and CT concentrations in the canal at the hypothetical reclaimed water discharge location are shown in Figure 3-31 for the four cases considered in the model and for the entire water quality simulation period. The concentrations of the microconstituent with the highest adsorption coefficient (TS) shows fewer fluctuations, which is likely a consequence of the adsorbed mass in the sediment layer acting as a buffer. The relative variation of the relative concentration in the last modeled year is plotted in Figure 34. The relative variatio decreases as the organic carbon partitioning coefficient increases. Clearly the value of the adsorption coefficient is a significant factor in determining how fast the concentrations change in the river network.

The total degradation rate of microconstituents computed by ECO Lab is similar to the one used for the overland flow (Appendix C, Table C.2), except for the correction of the

photolysis rate for the water depth and different wind velocities, which take place when calculating the evaporation rate. According to Figure 33, the concentration at the hypothetical reclaimed water discharge location stabilizes around a value that is correlated to the total degradation rate estimated for overland water in Table C.2. This dependency is better observed by plotting the mean annual value of the relative concentration and the total decay rate, as shown in Figure 34. As expected, the results show that the stabilized concentration the canal water column at the hypothetical reclaimed water discharge location is lower for microconstituents with higher total decay rate from all the degradation processes (reference Appendix C for further degradation process details).

Figure 3-34, Figure 3-35, and Figure 3-36 show the concentrations of microconstituents adsorbed in suspended particles, dissolved in the pore water of the sediment layer and adsorbed in the sediment layer, respectively.

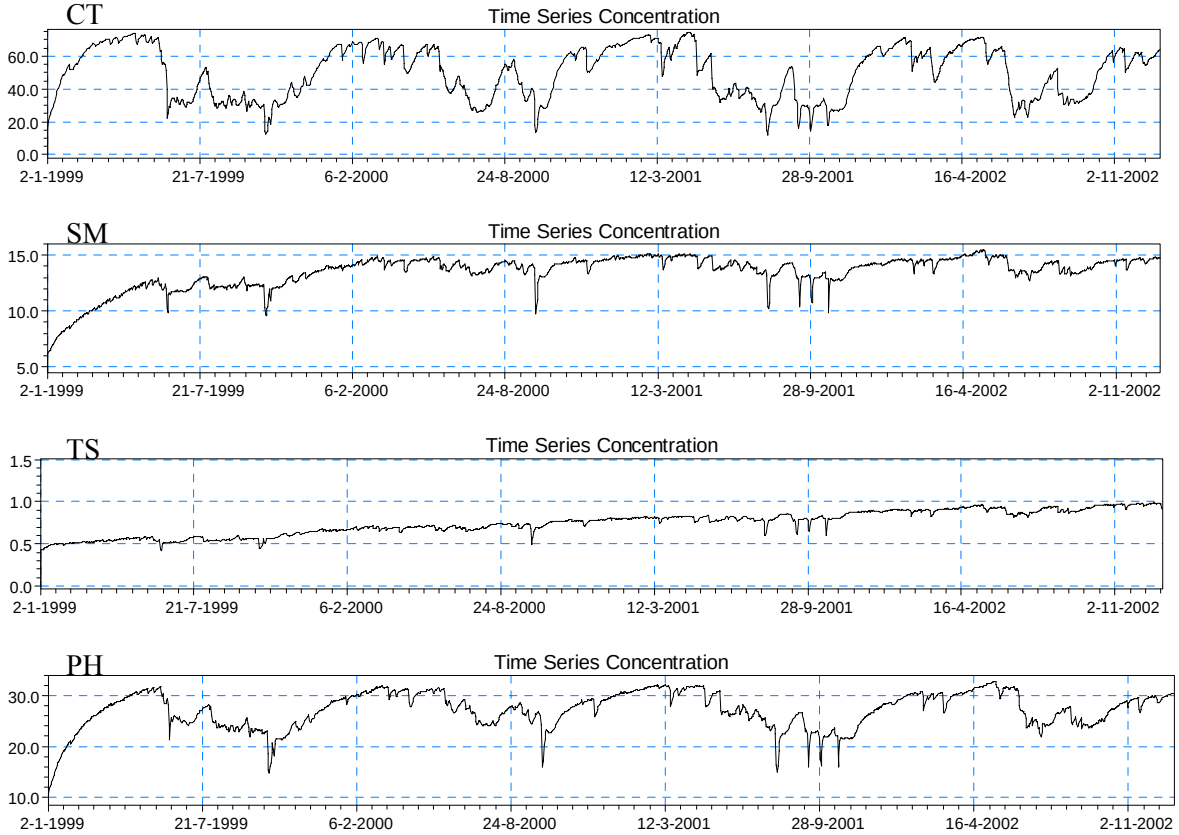


Figure 3-29.Simulated concentrations of dissolved microconstituents (micro-g/m^3) in the Holloway canal at WWTP effluent for the period of 1999-2002.

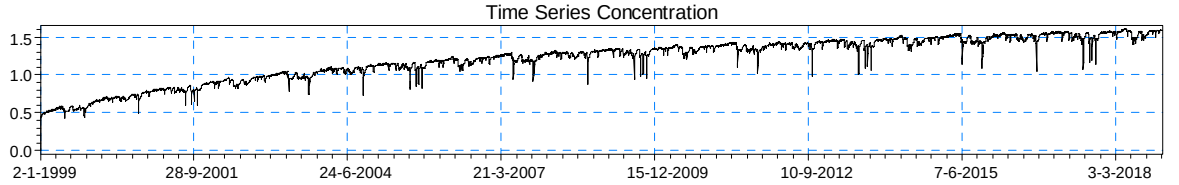


Figure 3-30.Simulated concentrations of dissolved TS (micro-g/m^3) in the Holloway canal at the hypothetical reclaimed water discharge location for the whole simulation period.

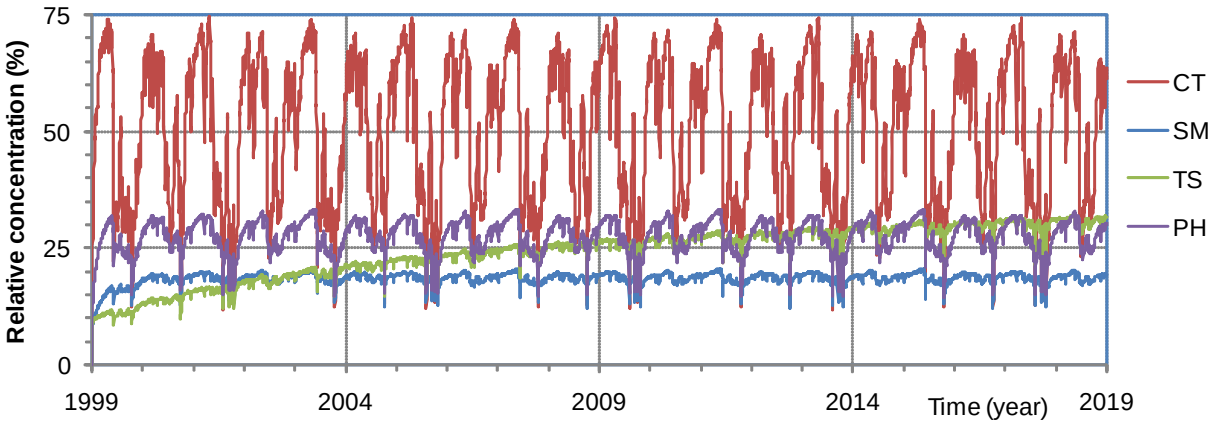


Figure 3-31.Simulated relative concentrations for all dissolved microconstituents in the Holloway canal at the hypothetical reclaimed water discharge location.

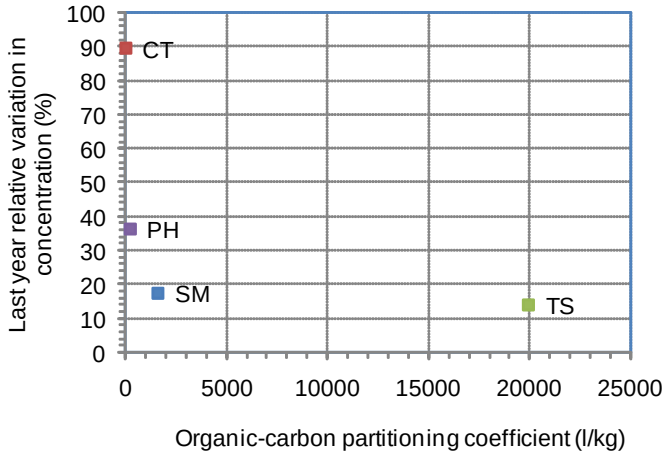


Figure 3-32.Annual relative variation of the concentration (maximum minus minimum, all divided by the mean value) as a function of the adsorption coefficient. The parameters were computed from the last year relative concentrations in the Holloway canal at the hypothetical reclaimed water discharge location presented on Figure 3-31.

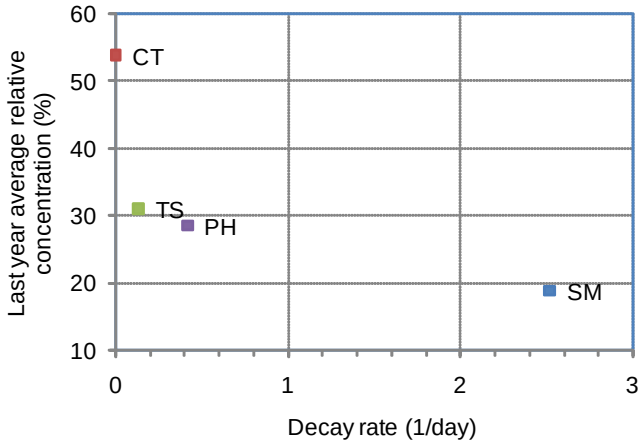


Figure 3-33.Relative concentration (maximum minus minimum, all divided by the mean value) as a function of the decay rate. The parameters were computed from the last year relative concentrations in the Holloway canal at the hypothetical reclaimed water discharge location presented on Figure 3-31.

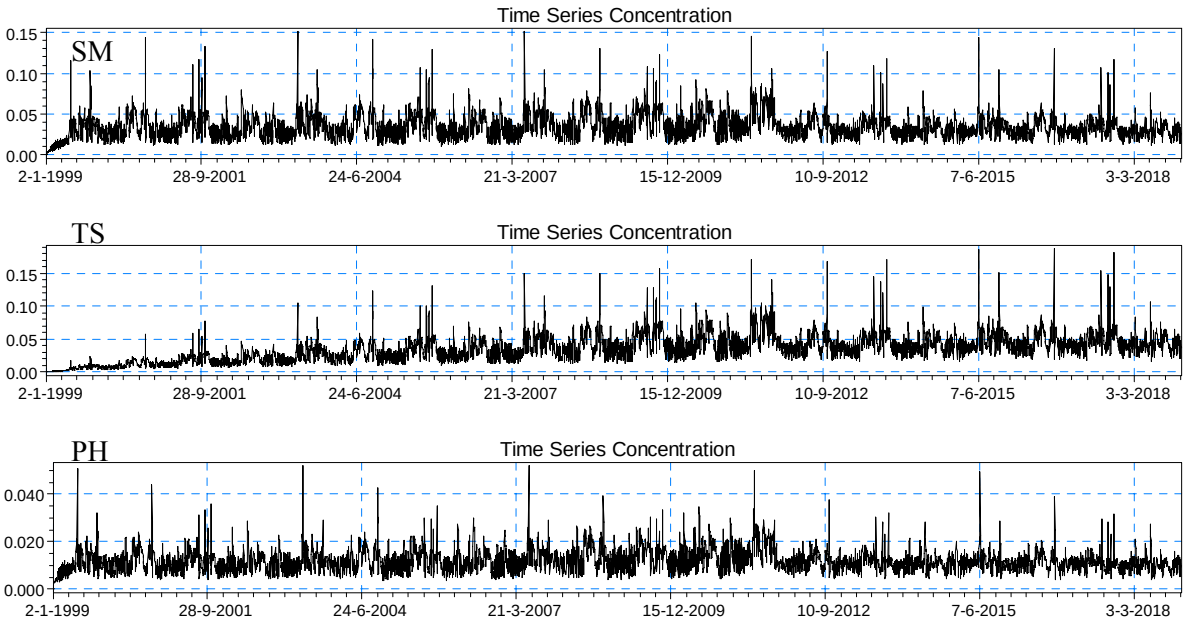


Figure 3-34.Simulated concentrations of adsorbed microconstituents in suspended sediments (micro-g/m^3) in the canal at hypothetical reclaimed water discharge location.

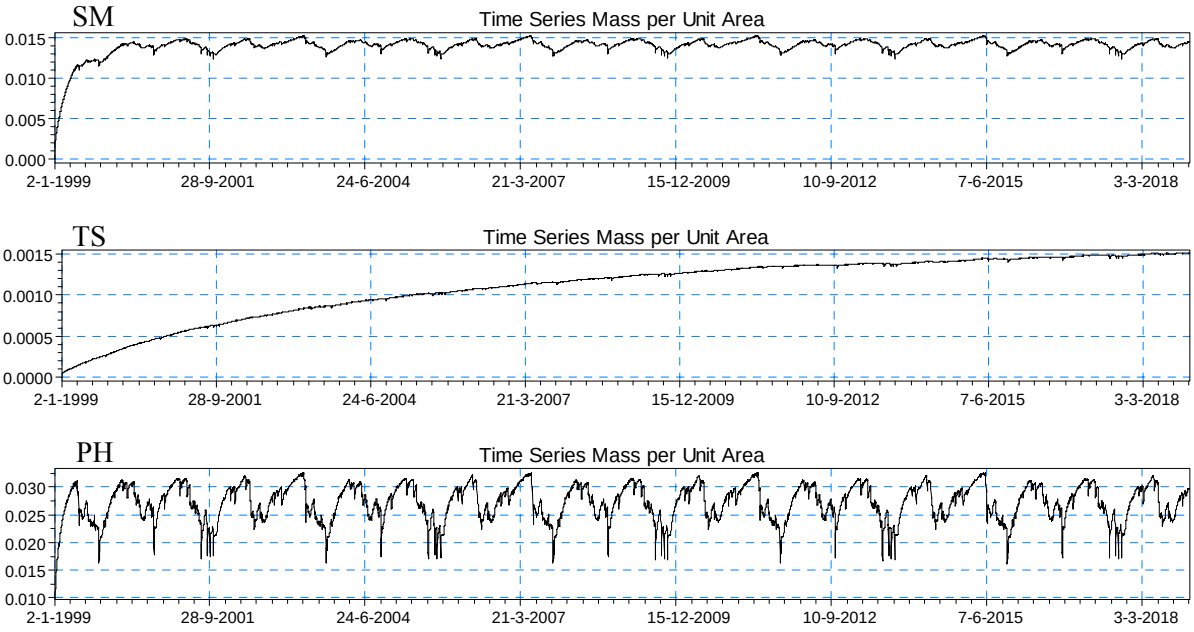


Figure 3-35.Simulated mass of dissolved microconstituents per unit area (mg/m^2) in the sediment layer pore water in the canal at the hypothetical reclaimed water discharge location.

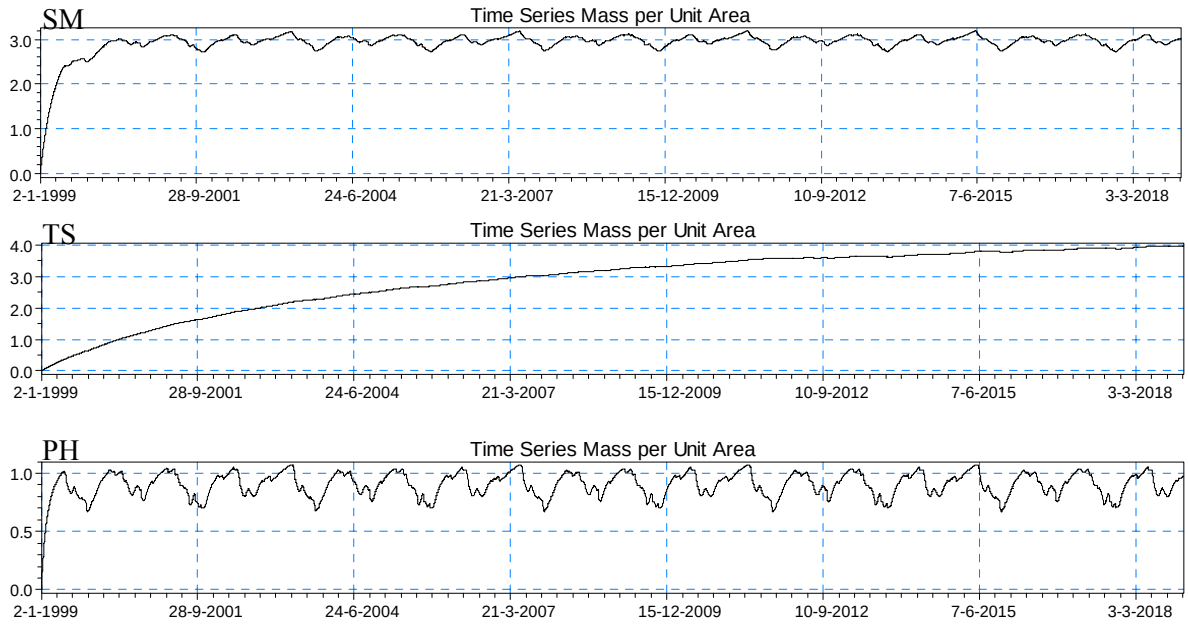


Figure 3-36.Simulated mass of adsorbed microconstituents per unit area (mg/m^2) in the sediment layer in the canal at the hypothetical reclaimed water discharge location.

The concentration of the dissolved microconstituents predicted by the model at the hypothetical reclaimed water discharge location decreases for deeper groundwater layers, as shown in Figure 3-37. In that figure, a logarithmic scale was used in order to display the small concentrations found in groundwater. It is clear from those graphs that adsorption plays an important role in the vertical variation of the concentration. Since the model assumes no degradation in groundwater layers, the mass of dissolved contaminants in cells with no extraction wells can be only transported by advection and diffusion processes and also adsorbed onto the soil porous surface depending on its adsorption coefficient value. Starting from a zero-concentration model causes the concentrations to increase systematically in groundwater cells. Thus, adsorption represents a sink in the dissolved mass balance equation; and a higher adsorption coefficient causes a slower spreading of the contaminant in the groundwater layers. As a result, the groundwater concentration at a given time is higher for the conservative tracer and lower for other microconstituents as the adsorption coefficient increases. For the microconstituents in the model, the adsorption coefficient increases in the following order: PH, SM and TS.

Groundwater microconstituent transport in the horizontal direction is illustrated on Figure 3-38. This figure shows the spatial distribution of the concentration for the conservative tracer and the three microconstituents for the groundwater Layer 3 at the end of the 20-year simulation period. The results are shown for Layer 3 because it is where most of the groundwater extraction occurs in the model. Notice that a linear colour scale for the concentration was used for CT and logarithmic ones otherwise. Similar to the vertical direction, the adsorption is important in the horizontal spreading of microconstituents. In the case of no adsorption (CT), the model predicts a wide plume shifted to the east from the WWTP effluent location and covering three of the four well fields. However, for the other three microconstituents, the higher concentrations are mostly detected below the canal branches and they are several orders of magnitude lower than the WWTP effluent concentration.

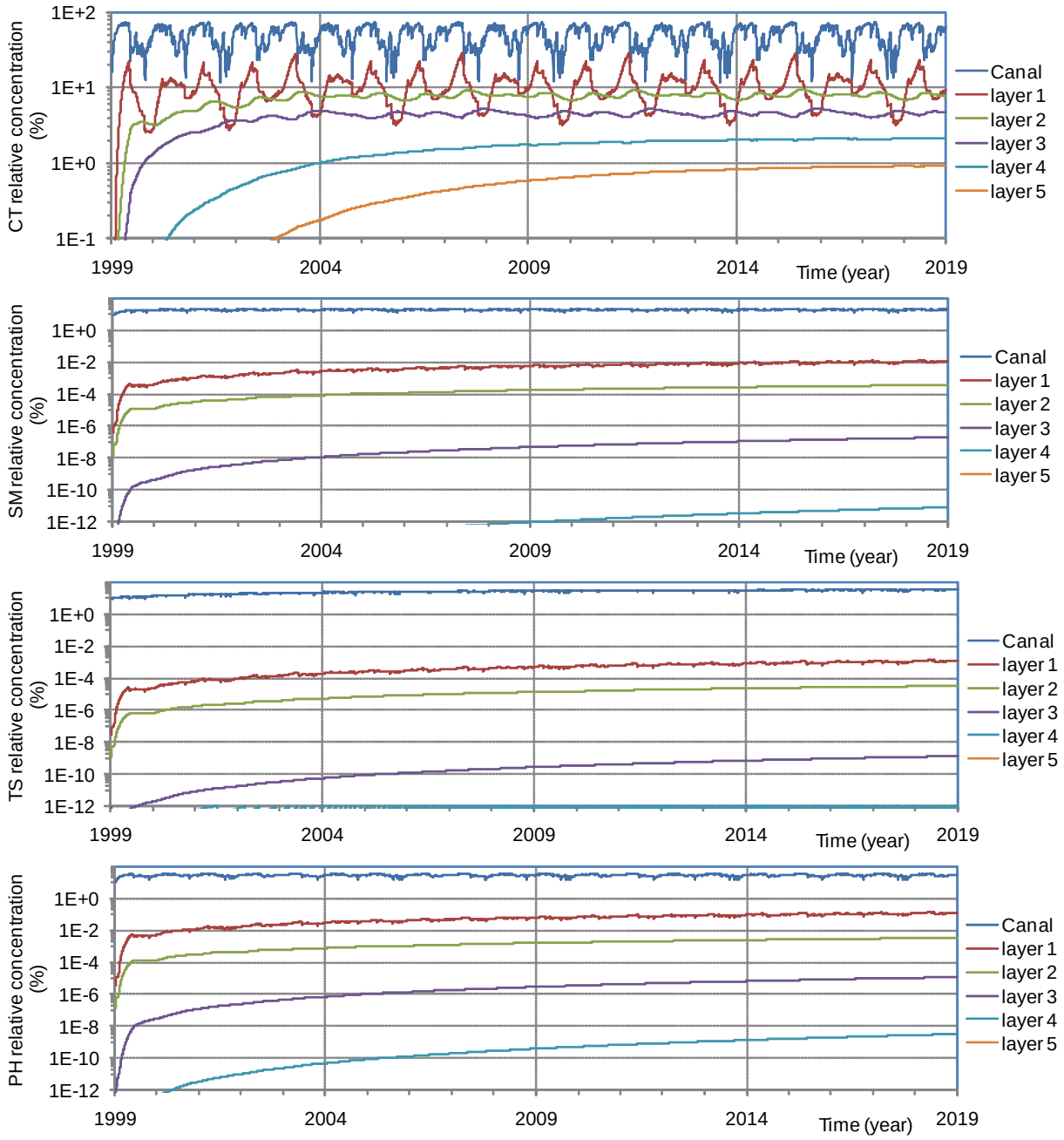


Figure 3-37.Evolution of the relative concentration at the hypothetical reclaimed water discharge location for the canal water and the different groundwater (computational) layers.

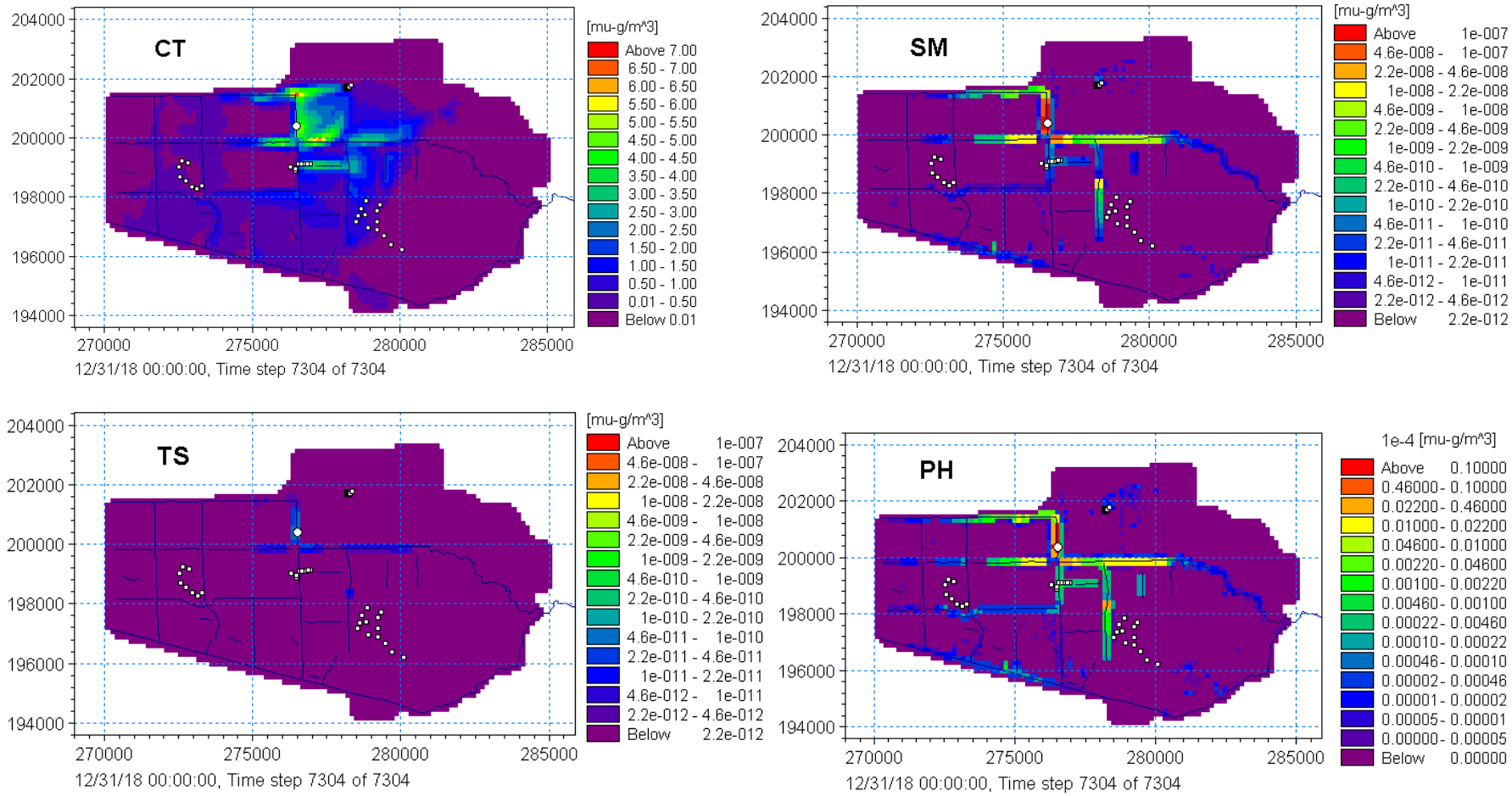


Figure 3-38.Simulated concentration of microconstituents (mu-g/m^3 = micro-g/m^3) in groundwater Layer 3 at the end of the 20-year simulation period. The white circle represents the WWTP effluent and the small white squares the extraction wells.

Finally, the distribution of the concentration of the different microconstituents in the river network is presented from Figure 3-39 to Figure 3-43.

Two dates at the end of the dry and the wet season of the last year of the simulation period were selected. The graphs illustrate that there are bigger differences in the concentration between the two dates for the CT case, where the adsorption coefficient is assumed negligible. Moreover, the spreading of the microconstituents in the river network is higher for CT and decreases for PH, SM and TS, in this order. This suggests that the spreading in the canal network is more influenced by the adsorption coefficient than by the total decay rate in the model conditions and within the simulation period (20-year) frame. In other words, this is a sign that the model may be still transiting from the zero-concentration conditions to stable concentration values. This is at least true for the TS.

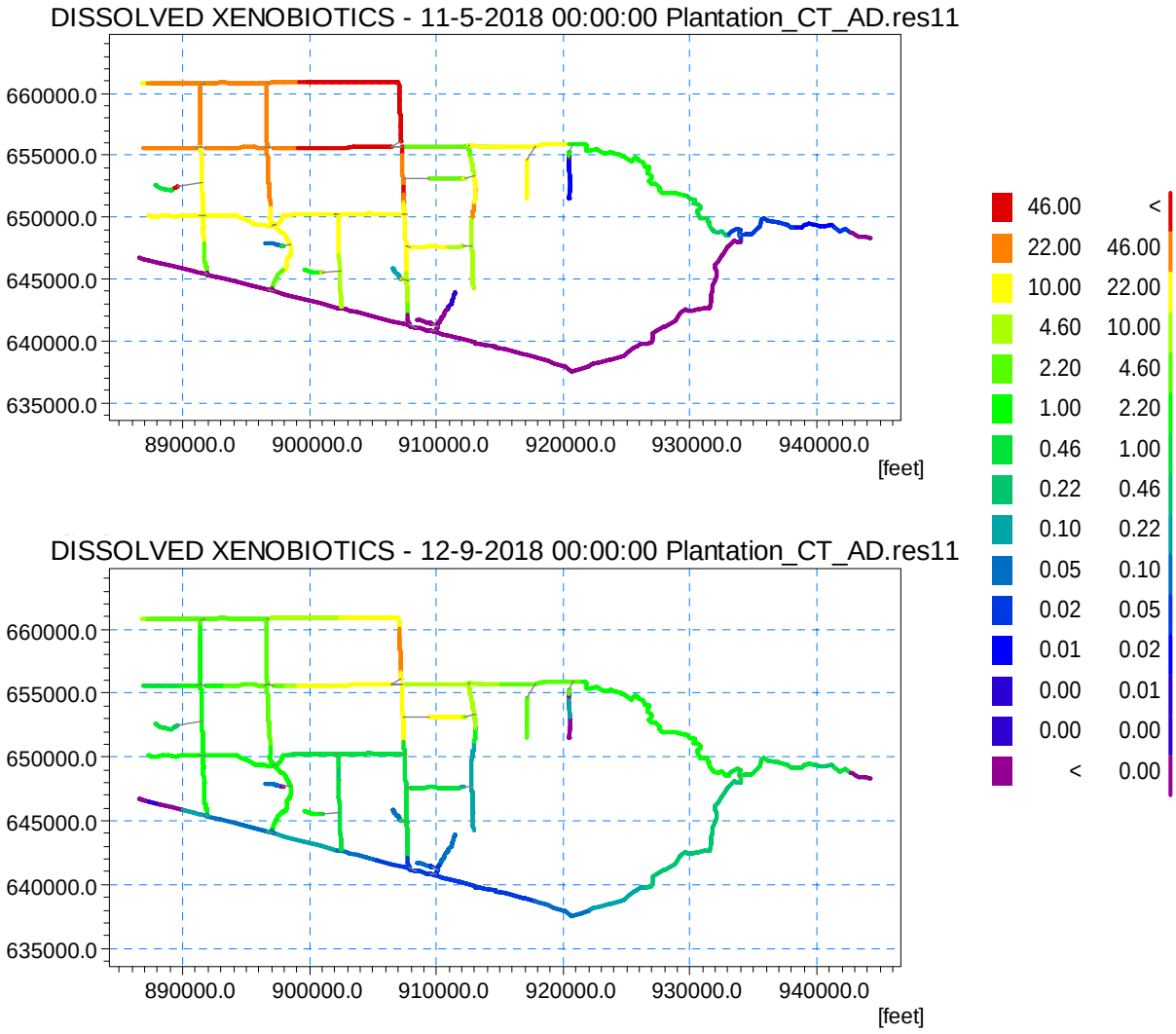


Figure 3-39.CT concentration (micro g/m^3) in the canal network on two dates during the last year of the simulation period.

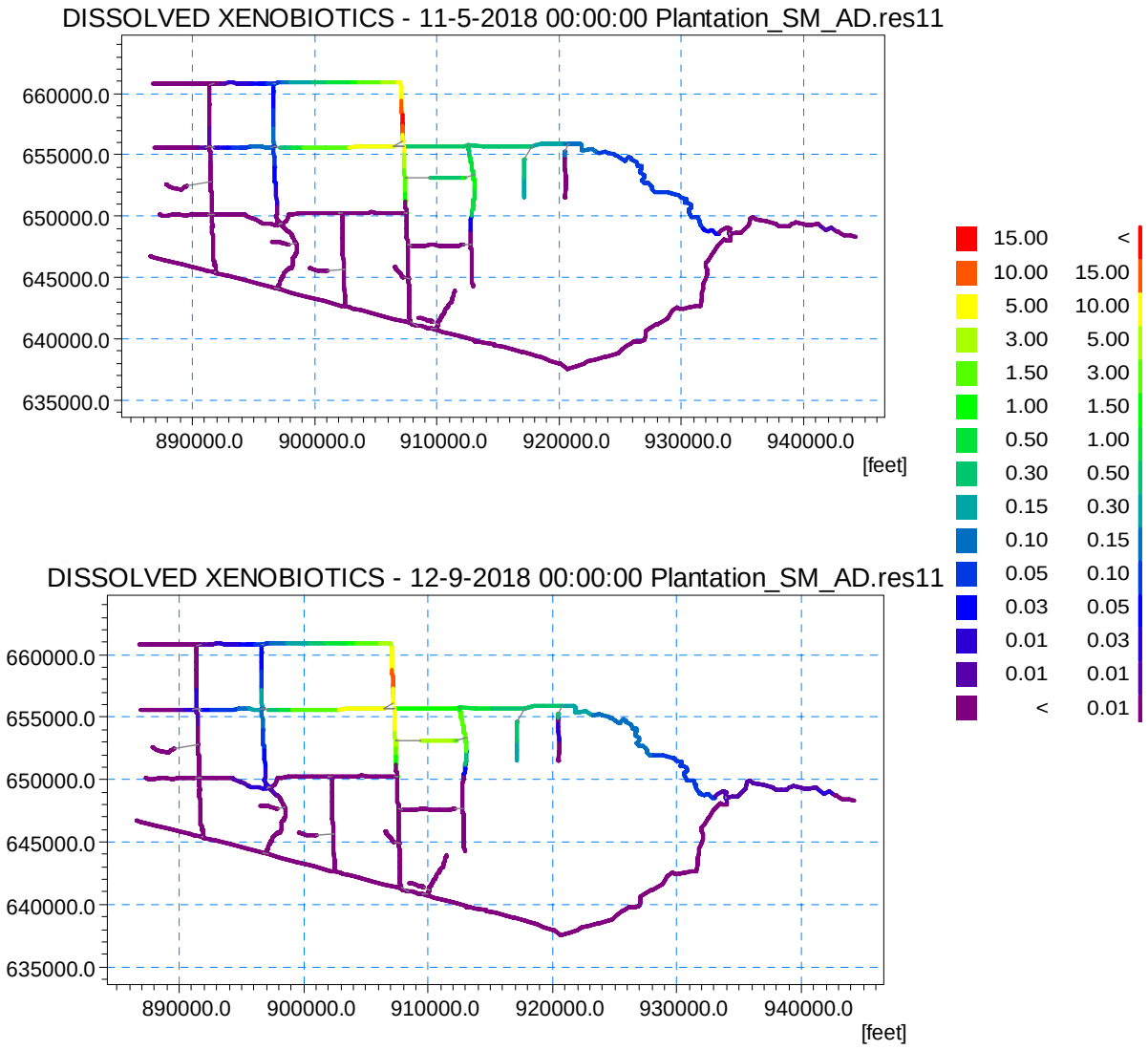


Figure 3-40.SM concentration (micro g/m^3) in the canal network on two dates during the last year of the simulation period.

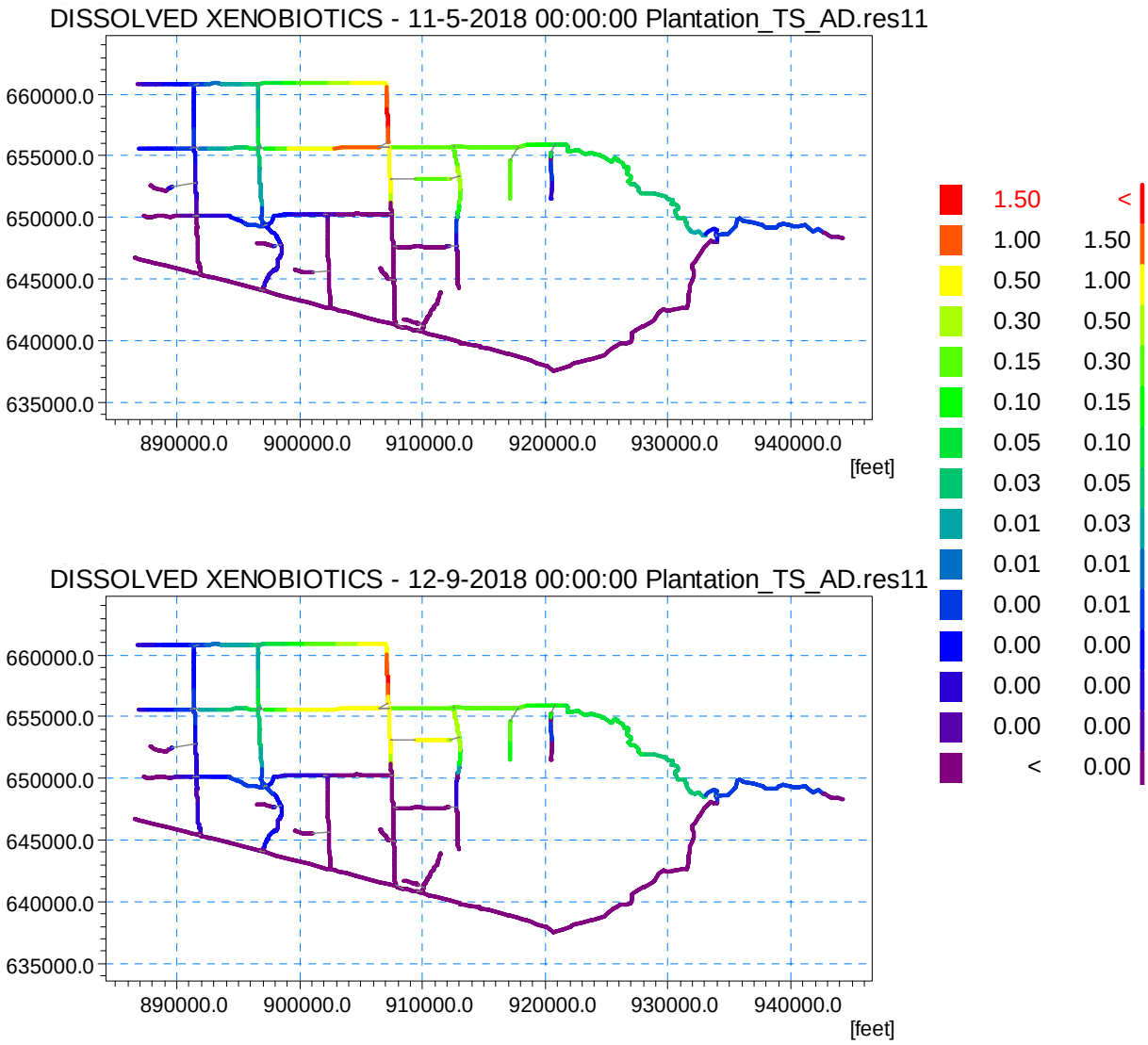


Figure 3-41.TS concentration (micro g/m^3) in the canal network on two dates during the last year of the simulation period.

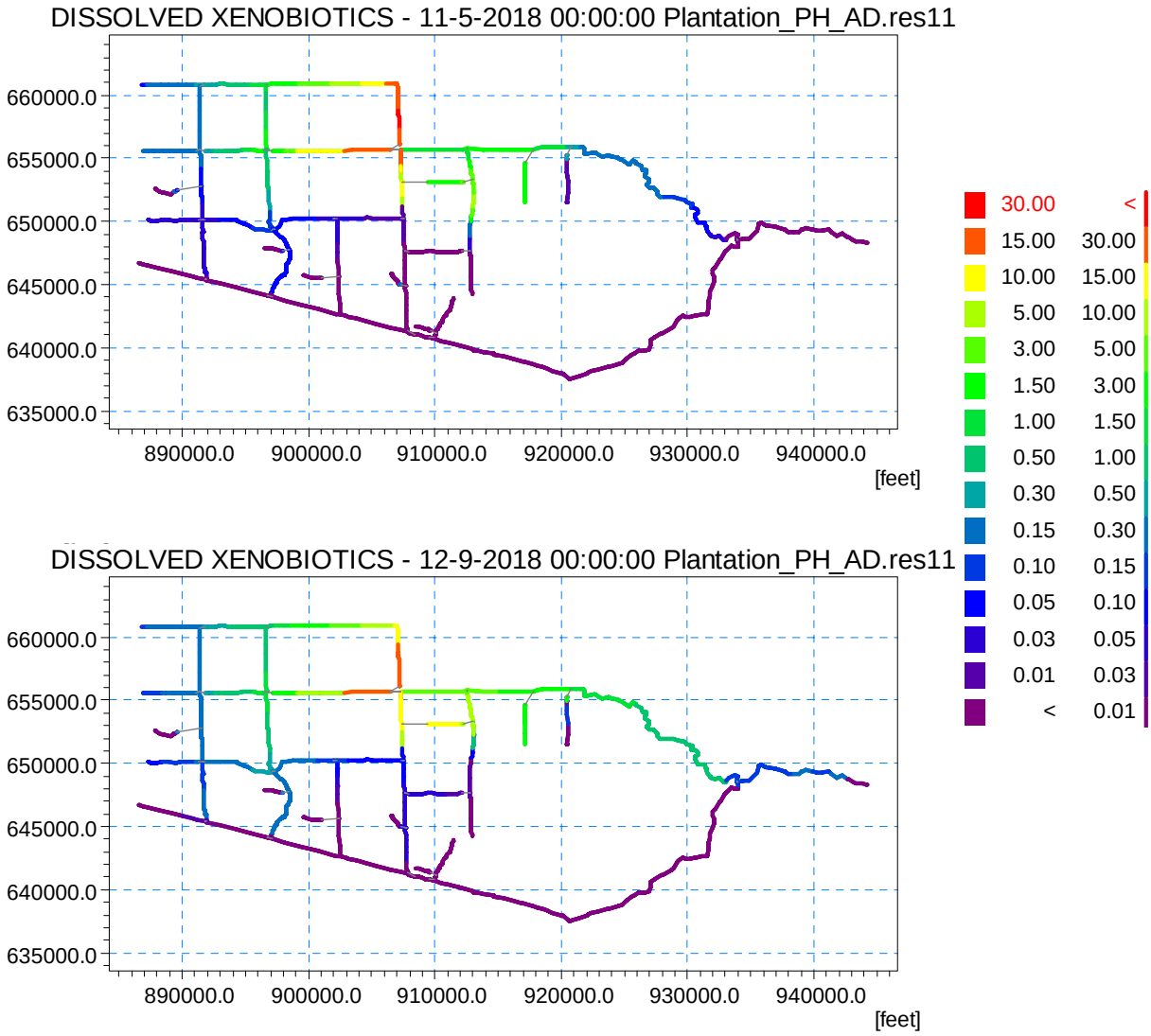
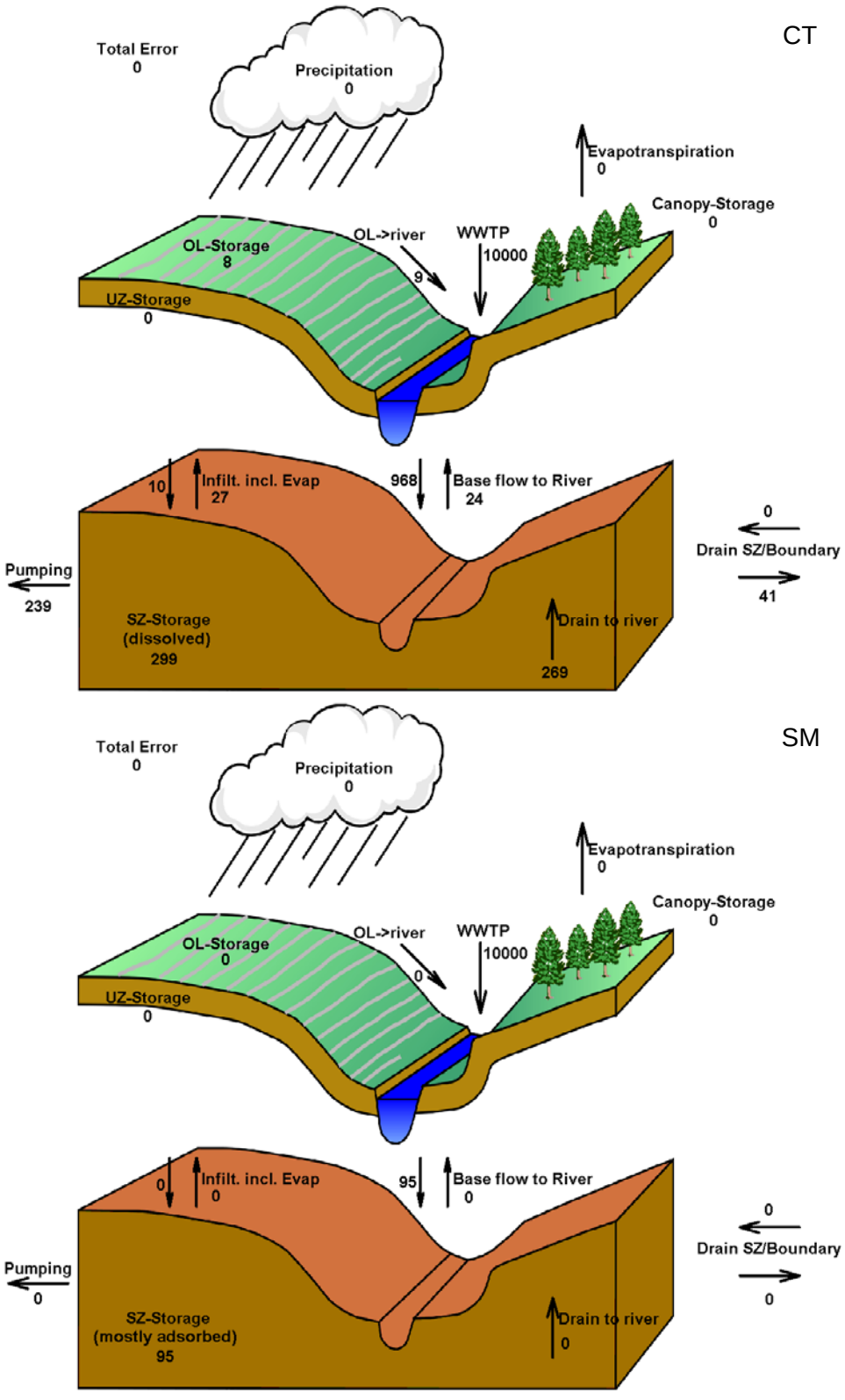


Figure 3-42.PH concentration (micro g/m^3) in the canal network on two dates during the last year of the simulation period.

Finally, a sketch of the mass balance for the entire MIKE SHE model domain for the last year of the simulation period is presented in Figure 45. The mass balance for CT reveals that the mass is more distributed in the model causing that 2.39 % of the mass discharged from WWTP is extracted in potable water supply wells. However, in the case of the other microconstituents this mass fraction is negligible. Another difference is that the mass stored in ground water layers during that period is dissolved for CT, but mostly adsorbed for the other three cases, where the dissolved amount is negligible. Finally, notice that the amount adsorbed in groundwater layer represent a mass fraction from 0.12 % to 2.41% and it is correlated to the adsorption coefficient for those three microconstituents.


CT
Total Error
0
Precipitation
0
Evapotranspiration
0
Canopy-Storage
0
OL-Storage
8
OL->river
9
WWTP
10000
UZ-Storage
0
10
Infilt. incl. Evap
27
968
Base flow to River
24
0
Drain SZ/Boundary
41
Pumping
239
SZ-Storage
(dissolved)
299
Drain to river
269
SM
Total Error
0
Precipitation
0
Evapotranspiration
0
Canopy-Storage
0
OL-Storage
0
OL->river
0
WWTP
10000
UZ-Storage
0
0
Infilt. incl. Evap
0
95
Base flow to River
0
0
Drain SZ/Boundary
0
Pumping
0
SZ-Storage
(mostly adsorbed)
95
Drain to river
0

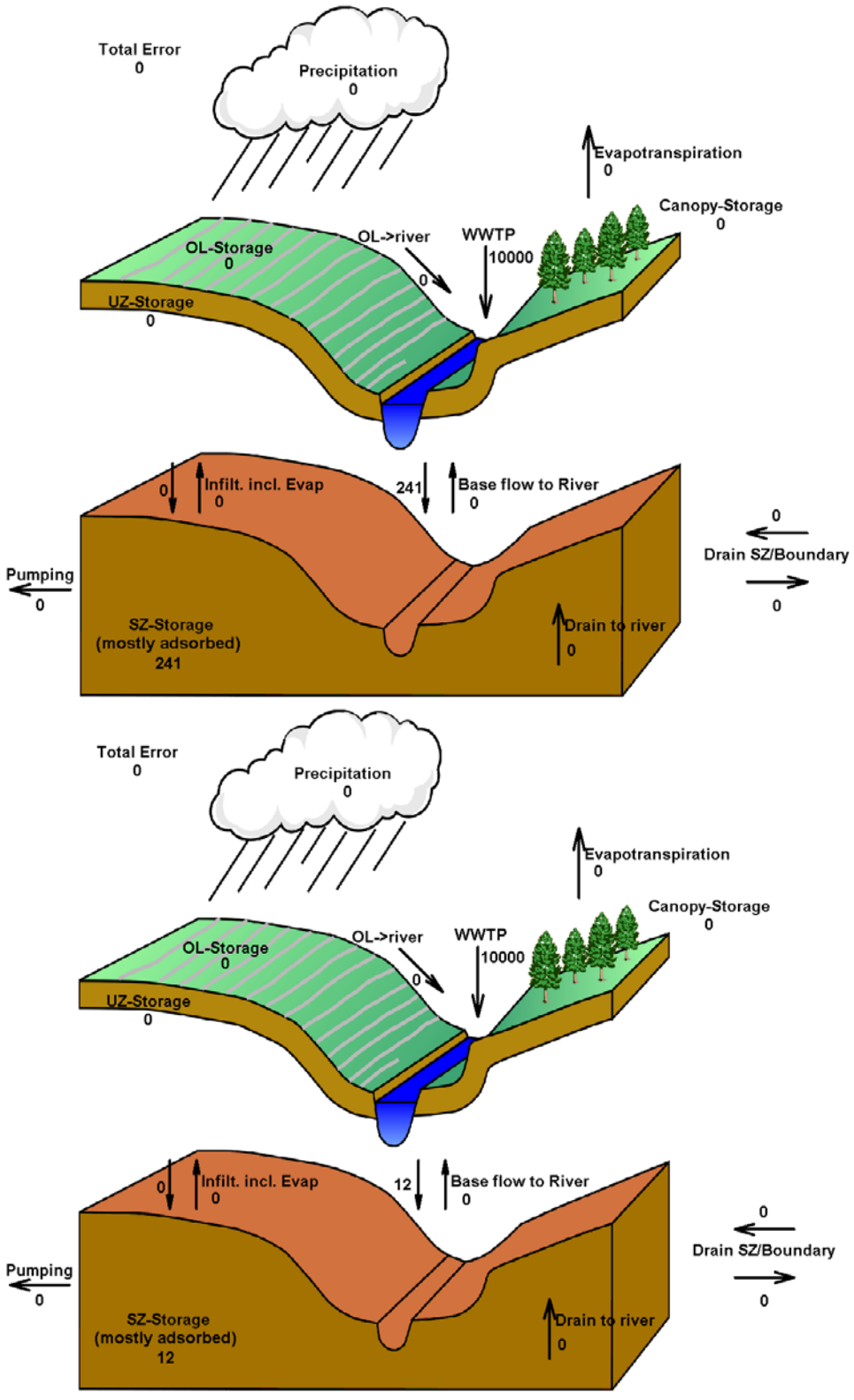


Figure 3-43.Mass balance for the conservative tracer and microconstituents models during the last year of the simulation. Values are in relative mass units assuming a value of 10000 discharged from WWTP into the river network during that period.

3.7.3. Conclusions

A water quantity and quality model was built to study the transport the microconstituents discharged from the City of Plantation AWT in the surface water canals and the Biscayne Aquifer. The water quality model developed predicts that adsorption plays an important role in the transport of the microconstituents in the canal network as well as in aquifer system. The model species sorted from lower to higher adsorption coefficients are CT, PH, SM and TS. Higher adsorption coefficient decreases the fluctuations in the dissolved concentration in the canals, which is likely a consequence of the adsorbed mass in the sediment layer acting as a buffer. For Triclosan, which has the highest adsorption coefficient, stable concentrations were reached in the Holloway (at the WTP effluent location) at the end of the simulation. These results confirm that the value of the adsorption coefficient influence how fast the dissolved concentration changes in the river network.

The spreading of the contaminant in the river network was found higher for lower adsorption coefficients. This is an indication that the river network may be still transiting from the zero-concentration condition to stable concentration values.

In groundwater, adsorption also plays an important role in the vertical and horizontal spreading of the contaminant. Higher adsorption coefficient causes a slower spreading of the microconstituents in the groundwater layers. For the microconstituents where adsorption is not neglected (PH, SM and TS), the concentration reduces in orders of magnitude from one ground water layer to a deeper one, in the 20-year simulation period. In the horizontal direction, the higher concentrations were obtained mainly below some the canal branches. Even so, the concentrations at extraction well depths (ground water layer 3 of the model or below) are several orders of magnitude lower than the one assumed from the WWTP effluent.

While the adsorption process reduce the speed of the concentration changes, the total degradation rate determine the typical concentration value obtained in the canal at the WWTP effluent at the end of the simulation period. In other words, the higher the total degradation rate at surface water caused by biodegradation, photolysis and evaporation the lower the typical concentration of the microconstituent in the canal network obtained after the period where adsorption rules the transition from the initial conditions.

3.7.4. Future work

The water quality model is not calibrated and a future effort should be focused on collecting the data necessary to perform calibration. It would be useful to obtain measurements of the water discharge rates from the WWTP as well as the concentration of the microconstituents of interest. In addition, measurements of the microconstituent concentrations in surface water canals and in groundwater observation and supply wells, the dissolved fraction and the suspended particle concentration at various canal locations and at different times would be also valuable for model calibration.

The model results from indicate that adsorption is the dominant process in the microconstituent spreading. Thus, further efforts can be directed to a better estimation of the related parameters such as mass organic fraction and bulk density in groundwater layers and in sediment layer.

Finally, the current model does not consider the suspended sediment transport in the water flow from the overland surface and drain features into the canals. Thus, surface runoff in the model provides sediment-free water to the canals neglecting overland erosion. This limitation can be removed by estimating time-varying sediment particle concentrations from the overland water inflow rates to the river network and setting them as boundary condition in MIKE11.

4. PROJECT CONCLUSIONS

This objectives of this study were to evaluate the removal of microconstituents through AWT facilities, investigate the potential impact of microconstituents to aquatic organisms, and examine the fate and transport of select microconstituents from a hypothetical canal discharge location to a drinking water aquifer with a hydrodynamic and water qulity model.

The results indicate that almost all microconstituents were effectively removed by RO in AWT facilities, and RO effluent posed no hormonal threat to tissue cultures and live fish. The observed toxicity to aquatic organisms was likely caused by chloramines for membrane maintenance but not microconstituents. Furthermore, toxicity was significantly reduced after quenching (dechlorination) of chloramine. Hydrodynamic models and water quality models can help us evaluate the fate and transport of microconstituents and impact of discharged reclaimed water.

4.1. Aquatic and Human Health Impact Potential

Microconstituents can originate from numerous sources and enter the environment by many routes, and occur in WWTP effluents, surface water, ground water, reuse water, and drinking water, although their concentrations are usually in the ng/L range. However, some microconstituents at or above 0.1 ng/L may cause endocrine disruption in fish and other aquatic life (Purdom et al., 1994; Vanderford, 2003), but there is little evidence to suggest that typical low-level environmental exposures to microcontituents have had any adverse effect on human health (WHO, 2002). The long-term human health impact of trace level microconstituents deserves further investigation.

4.2. Microconstituent Removal

The results of microconstituent removal indicated that select microconstituents may pass through RO membranes at very low levels, although most microconstituents were completely removed with RO membranes. Thus, it is prudent to consider further reduction of microconstituents through biological (as part of secondary treatment) or chemical oxidation processes. Please note numerous processes exist beyond those demonstrated here. The microconstituent removal efficiency of nine treatment processes were reviewed in this report as follows: conventional activated sludge, coagulation, activated carbon adsorption, membrane bioreactor, O_3/H_2O_2/UV oxidation, chlorination, membrane filtration, enzymatic treatment, and ferrate (VI) oxidation. Most of these processes can effectively remove microconstituents, for example, advanced oxidation technologies are well proven to destroy microconstituents that may pass through RO systems.

All three systems (MBR/RO, DNF/UF/RO, IMANS) in this project effectively removed microconstituents and reduced BOD_5, TSS, TDS, and tubidity. The BOD_5 of most MBR effluents and UF effluents were below detection limits (2 mg/L) and the BOD_5 of all RO effluents were below detection limits. The TSS of MBR effluents, UF effluents, and RO effluents were all below detection limits (1 mg/L). The TDS of MBR effluents, UF effluents, and RO effluents were all below 0.88 NTU. Compared with canal water, the water quality of RO effluent in AWT facilities was higher. The TSS, BOD_5, and turbidities in RO effluents were all below 1 mg/L, 2 mg/L, and 0.44 NTU, respectively. These numbers were much lower than those of the canal water (TSS: 7.0 mg/L; BOD_5: 5.27 mg/L; 7.67 NTU). In addition, the particle size distributions of RO effluents were not significantly different from those of distilled water using statistical Student t-test. All of these results suggest that the discharge of reclaimed RO water may not deteriorate water quality of surface canals, and any of the three tested systems can be used to remove microconstituents and improve the quality of reclaimed water for canal discharge.

4.3. Toxicity Testing

The chronic toxicity tests include chronic survival and growth test of *P. promelas* and chronic survival and reproduction test of *C. dubia*. The survivability of *P. promelas* and *C. dubia* in RO effluent were low during the first toxicity test, which was likely caused by chloramine in RO effluent. Additional tests on RO effluent samples that were quenched with sodium thiosulfate significantly reduced toxicity and increased the survivability of *P. promelas* and *C. dubia* in RO effluents. The final batch of toxicity experiments without chloramine indicated that there was no significant difference in RO effluent and control (de-ionized) water for the survival and growth *P. promelas* and survival and reproduction of *C. dubia*. Similarly, there were no significant differences in surface (canal) water and control (de-ionized) water for the survival and growth *P. promelas* and survival and reproduction of *C. dubia*. These fact suggest that discharge of reclaimed water (RO effluent) has no adverse toxic effect on aquatic organisms. However, unquenched chloramines or trace level of ammonia in AWT facilities may contribute to the toxicity to *C. dubia* and should be removed by break point dechlorination, advanced oxidation, or other quenching methods, and deserves further investigation.

4.4. *In Vivo* and *In Vivo* Testing

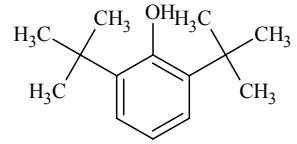
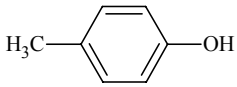
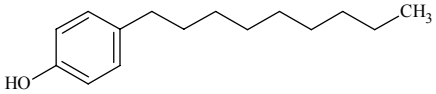
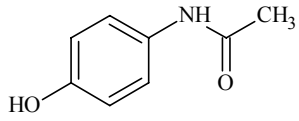
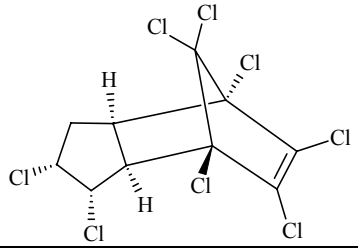
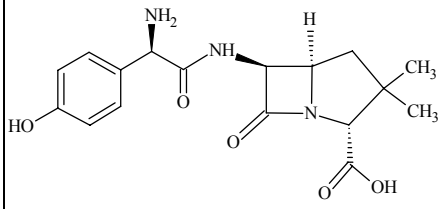
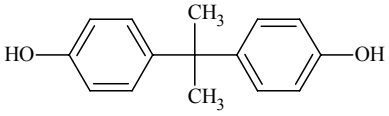
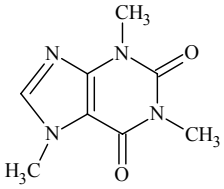
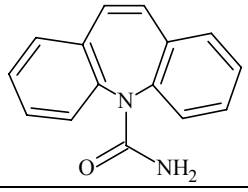
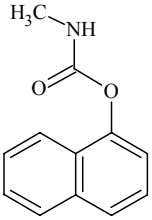
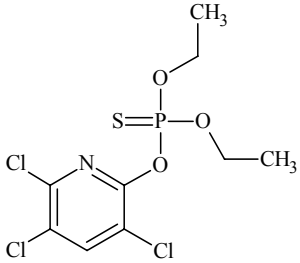
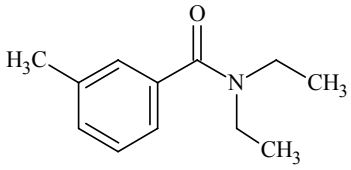
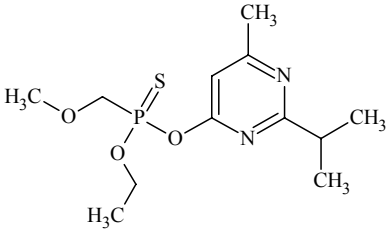
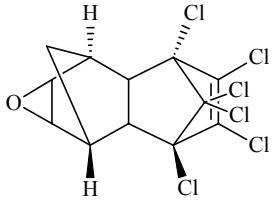
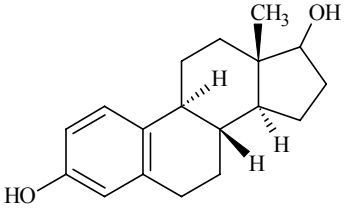
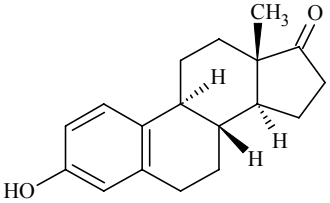
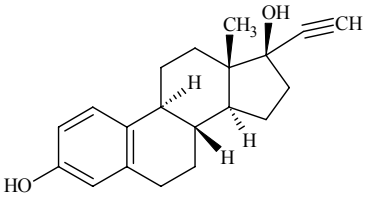
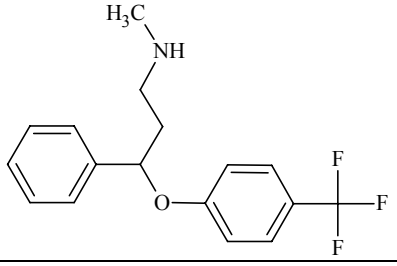
The endocrine disrupting potential of microconstituents in RO effluent were evaluated with E-Screen bioassay, YES assay, fathead minnow Vtg assays and steroid immunoassays. The results of E-Screen bioassay indicate that estradiol equivalents in all RO effluents were below detection limits, even though estradiol equivalents were detected in secondary effluent, DNF effluent, MBR effluents, and UF effluents. The results of E-Screen bioassay indicate that RO effluent did not provoke a significant response in MCF-7 cells. The results of YES bioassay were similar to those of E-Screen bioassays and estradiol equivalents in RO effluents were below detection limits although estradiol equivalents were detected in secondary effluent and DNF effluent, suggesting that RO effluent didn't possess endocrine disrupting potential. The results of fathead minnow Vtg assays and steroid immunoassays did not show an increase of plasma Vtg in male fish, indicating that they are not exposed to estrogenic components at the required concentrations for this effect. The results of steroid immunoassays indicated that testosterone concentrations in all treatments were similar to those in the negative control group and there was no significant difference in plasma testosterone for any of the treatments compared to negative controls. All of these results suggest that RO effluents were not estrogenic.

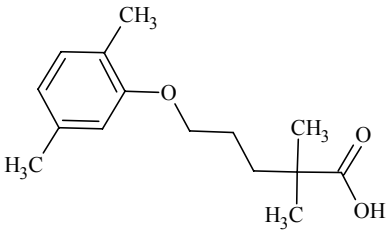
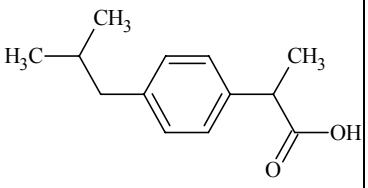
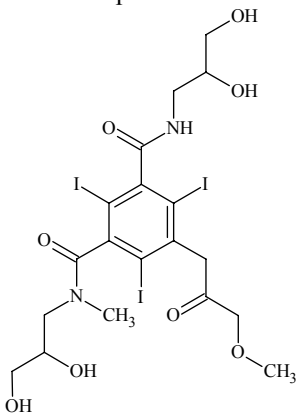
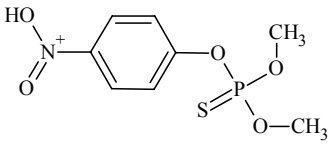
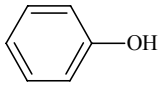
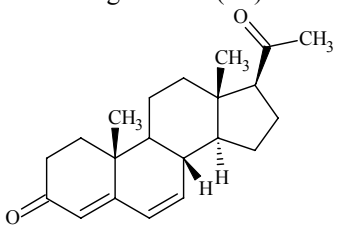
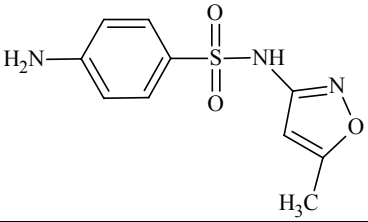
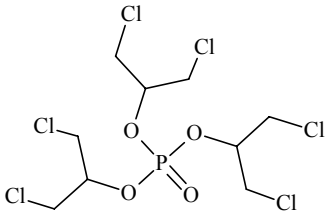
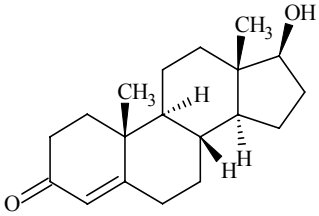
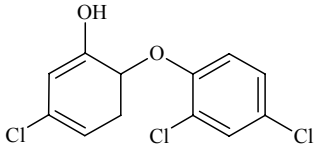
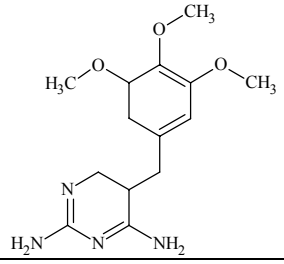
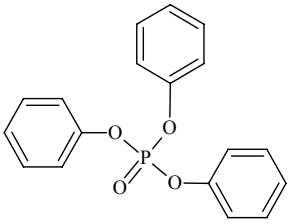
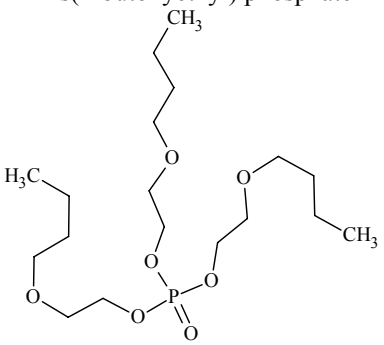
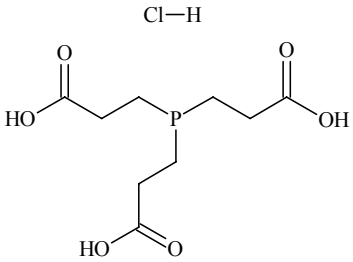
4.5. Modeling Results

Three microconstituents (sulfamethoxazole, triclosan, phenol) out of six reviewed representative microconstituents were selected for model development based on their physical/chemical properties. Hydrodynamic and water quality models were developed to examine the fate and transport of these simulated microcroconstituents from the AWT through surface canals. The hydrodynamic model was run for a two-year period (2001 - 2002) and the results indicated that the groundwater results follow the observed data closely, but the surface water results are very sensitive to the structure operations. The water quality model developed predicts that adsorption plays dominant role in the transport of the microconstituents in the canal network as well as in aquifer system. While less significant, various pathways of decay do impact fact and transport of microconstituents. The spreading of microconstituents in the canal network was found to be less for compounds with higher adsorption coefficients. The higher adsorption coefficient decreases the fluctuations in the dissolved concentration in the canals, which is likely a consequence of the adsorbed mass in the sediment layer

acting as a buffer. These results confirm that the value of the adsorption coefficient influence how fast the dissolved concentration changes in the canal network. The water quality model is not calibrated and a future effort should be focused on collecting the data necessary to perform calibration. Further efforts can be directed to a better estimation of the related parameters such as mass organic fraction and bulk density in groundwater layers and in sediment layer.

APPENDIX A
CHEMICAL STRUCTURES OF EXAMINED MICROCONSTITUENTS

2,6-di-tert-butylphenol 	4-Methyl phenol 	4-Nonyl phenol 
Acetaminophen 	Alpha chlordane 	Amoxicillin 
Bisphenol A (BPA) 	Caffeine 	Carbamazepine 
Carbaryl 	Chlorpyrifos 	N,N-diethyl-m-methylbenzamide (DEET) 
Diazinon 	Dieldrin 	Estradiol (E3) 
Estrone (E1) 	Ethynyl estradiol 17-alpha (EE2) 	Fluoxetine 

Gemfibrozil 	Ibuprofen 	Iopromide 
Methyl parathion 	Phenol 	Progesterone (PS) 
Sulfamethoxazole 	Tris(1,3-dichloro-2-propyl) phosphate (TDCPP) 	Testosterone 
Triclosan 	Trimethoprim 	Triphenyl phosphate 
Tris(2-butoxyethyl) phosphate 	Tris(2-chloroethyl) phosphate 	

Notes:
1. PubChem database from National Center for Biotechnology Information (http://pubchem.ncbi.nlm.nih.gov/)

APPENDIX B
MICROCONSTITUENT PROPERTIES FOR RECHARGE MODELING

Compound	Sulfamethoxazole	
CAS	723-46-6	
Aerobic Degradation	Sulfamethoxazole is biodegradable under aerobic conditions in an adapted activated sludge culture. Lag period before initiation of degradation was 4 days (Drillia et al., 2005). 32% to 49% was removed during secondary treatment. Tertiary treatment by sand filtration (Hydraulic retention time 25 min) did not affect the concentration (Göbel et al., 2007). In labstudies no significant biodegradation was found in pond water over a period of 30 days (Lam et al., 2004). A field investigation showed that 4 of 54 studied pharmaceuticals and personal care products were found below a treated sewage infiltration site (45 years of operation). Three m below the ground water table (unsaturated zone 1.5 - 2 m) sulfamethoxazole concentrations were between 0% and 20% of input concentrations (Ternes et al., 2007).	
Anaerobic Degradation	NA[1]	
Photolysis Degradation	Sulfamethoxazole (SMX) in its nonionized form in aqueous solution has ultraviolet (UV) adsorption that is maximal at 268 nm but extends through the ultraviolet B region (Moore and Zhou, 1994). Half lives in synthetic field water between 2.7 and 6.6 hours depending on the DOM content (Lam and Mabury, 2005) Mean half live in 12 m^3 microcosms with fish, aquatic plants, zooplankton, phytoplankton, macrophytes, and bacteria was 19 days (Lam et al., 2004)	
Hydrolysis	NA[1]	
Chemical behavior	Kd	NA[1]
	Koc	NA[1]
	Log Kow	0.89[2]
	H	
	pKa	6[2]
Notes: 1. NA: not available 2. Hazardous Substance Data Bank http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB		

Compound	Triclosan	
CAS	3380-34-5	
Aerobic Degradation	Aerobic biodegradation in soil 17.4 - 35.2 day half life (Morrall et al., 2004). A study designed to determine the die-away rate of triclosan released into a river as part of the sewage treatment plant effluent matrix determined a first order loss rate from measured data of 0.06 h^{-1}. Mathematical modeling indicated that sorption and settling accounted for approximately 19% of total triclosan loss over 8 km. When removing sorption and settling, the remaining amount of triclosan had an estimated first order loss rate of 0.25 h^{-1} (Morrall et al., 2004).	
Anaerobic Degradation	Triclosan is not readily or inherently degradable in standardised screening tests like OECD 301C (MITI I) or OECD 302C (MITI II). The negative results in these tests may be a consequence of the bacterial toxicity of Triclosan at the high substrate concentration required for these biodegradability screening tests (Samsøe-Petersen et al., 2003).	
Photolysis Degradation	Aqueous photolysis 41 min. half-life at pH 7 and 25°C (Samsøe-Petersen et al., 2003). Environmental Abiotic Degradation: The rate constant for the vapor phase reaction of triclosan with photochemically produced hydroxyl radicals has been estimated as $1.6X10^{-11}$ cu cm/molecule-sec at 25 deg C using a structure estimation method. This corresponds to an atmospheric halflife of about 8 hours at an atmospheric concentration of $5*10^{+5}$ hydroxyl radicals per cu cm. A direct photolysis rate of 0.07/day was measured using a water sample from the Greifensee, Switzerland tested under laboratory conditions, corresponding to a photolysis half-life in water of 10 days; the elimination rate sum of different transport and transformation processes in this lake is 0.03/day, corresponding to a half-life of 21 days[1]	
Hydrolysis	Triclosan is stable against hydrolysis in the environment due to its stability against strong acids and bases[2]	
Chemical behavior	Kd	NA[2]
	Koc	47454 mL/g (Morrall et al., 2004)
	Log Kow	4.8 (Morrall et al., 2004)
	H	NA[2]
	pKa	7.9[1]
Notes: 1. Hazardous Substance Data Bank, http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB 2. NA: not available		

Compound	Ibuprofen	
CAS	15687-27-1	
Aerobic Degradation	OECD Guideline 301B "Ready Biodegradability" Modified sturm test (CO_2 evolution) degraded after 28 d. Aerob; activated sludge, 20 mg/L: 10-60% [1]. A half-life of 20 days was determined from a study using water samples from lake Greifensee, Switzerland that were incubated at room temperature for 37 days with 200 ng/l racemic ibuprofen.[3] A field investigation showed that 4 of 54 studied pharmaceuticals and personal care products were found below a treated sewage infiltration site (45 years of operation). Three m below the ground water table (unsaturated zone 1.5 - 2 m) ibuprofen was undetectable. Input concentrations were in the range of 0.1 µg/l (Ternes et al., 2007).	
Anaerobic Degradation	NA[2]	
Photolysis Degradation	Ibuprofen is not expected to directly photolyze due to the lack of adsorption in the environmental UV spectrum (>290 nm).[1] The rate constant for the vaporphase reaction of ibuprofen with photochemicallyproduced hydroxyl radicals has been estimated as $1.2*10^{-11}$ cu cm/molecule-sec at 25 deg C. This corresponds to an atmospheric half-life of about 32 hours at an atmospheric concentration of $5*10^{+5}$ hydroxyl radicals per cu cm.[1]	
Hydrolysis	Carboxylic acids are generally resistant to hydrolysis. Therefore, hydrolysis is not expected to be an important removal process of ibuprofen from water systems.[2]	
Chemical behavior	Kd	NA[2]
	Koc	398[3]
	Log Kow	3.94 at 37 ºC[1], 3.97[4]
	H	NA[2]
	pKa	4.54 at 25 ºC[1], 4.91-5.2[4]

Notes:
1. ESIS: European chemical Substance Information System, http://ecb.jrc.it/esis/
2. NA: not available
3. Estimated with SRC's Pckoc Program
4. Hazardous Substance Data Bank, http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB

Compound	4 nonyl-phenol	
CAS	104-40-5	
Aerobic Degradation	Biodegradation of p-nonyl-phenol will occur rapidly in aerobic soils, but is inhibited in anaerobic soil conditions.[1] Degradation of 4-n-nonylphenol has been investigated in the laboratory using sediment and groundwater from an aquifer in Bolivar, South Australia. 4-n-NP degraded quickly under aerobic conditions with a half-life of 7 days (Ying et al., 2003).	
Anaerobic Degradation	See above	
Photolysis Degradation	Environmental Abiotic Degradation: p-nonyl-phenol should not be susceptible to direct photolysis based upon its lack of adsorption of light at wavelengths >290 nm. [1] Nonyl phenol is susceptible to indirect photolysis. The rate depends on initial concentration, pH, temperature, H_2O_2, Fe^{3+} and DOM. Half-lives in samples of the River Rhine and Hohloh Lake irradiated in a solar UV simulater were 30 days and 178 days (Neamtu and Frimmel, 2006). Sunlight phototransformation of NP was performed in quartz tubes which were suspended in a shallow flat-bottomed container filled with tap water or in Chriesbach creek. Half-lives of 10-15 hours under continuous clear sky, noon, summer sunlight in the surface layer of natural waters was found in the surface. At a depth of 20-25 cm half-lives were 1.5 times longer (Ahel et al., 1994).	
Hydrolysis	NA[2]	
Chemical behavior	Kd	NA[2]
	Koc	32400[3]
	Log Kow	5.76
	H	$3.4X10^{-5}$ atm-cu m/mole[1]

Notes:
1. Hazardous Substance Data Bank, http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB
2. NA: not available
3. Estimated with SRC's Pckoc Program, based on log Kow

Compound	Methyl parathion	
CAS	298-00-0	
Aerobic Degradation	Half-lives in river sediments between 3 and 6 days. Studies in 5 different soils showed half-lives between 3.5 days and 18 days. Same soils water logged indicating anaerobic conditions showed half-lives between 2.3 and 22 days in four soils and 275 days in the 5th soil.[1]	
Anaerobic Degradation		
Photolysis Degradation	Direct photolysis does not appear to be a significant transformation process in soils. Photolysis studies of methyl parathion have been reported. A study examining the photo-degradation of methyl parathion in river and seawater at variable temperatures showed the half-lives to be 11 and 34 days, respectively. In a photolysis study of methyl parathion in fresh waters of Portugal, a half-life of 3 days in groundwater and a half-life of 4 days in river water were observed.[2]	
Hydrolysis	Methyl parathion is rapidly degraded in natural water systems. The degradation of methyl parathion occurs much more rapidly in alkaline (pH 8.5) than in neutral (pH 7) or acidic (pH 5) conditions (Badawy and el-Dib, 1984). A hydrolysis half-life of 72-89 days was calculated for fresh water at 25 ºC and pH < 8 (EPA, 1978; Mabey and Mill, 1978) compared with about 4 days at 40 ºC and pH 8 (EPA, 1978).[2] The degradation of methyl parathion by hydrolysis and biodegradation was studied in four types of water (ultrapure water, pH 6.1; river water, pH 7.3; filtered river water, pH 7.3; and seawater, pH 8.1) maintained at 6 and 22 ºC, in the dark. The half-lives of methyl parathion at 6 ºC in the four water types were determined to be 237, 95, 173, and 233 days, respectively, and the half-lives at 22 ºC were determined to be 46, 23, 18, and 30 days, respectively. The study shows that degradation rates increase with pH and temperature, and are fastest in river water.[2]	
Chemical behavior	Kd	NA[3]
	Log Koc	2.7[2]
	Log Kow	2.86[2]
	H	$6.2x10^{-6}$ - $4.4x10^{-7}$ atm m^3/mol[2]
	pKa 3,5	3.8[4]

Notes:
1. Hazardous Substance Data Bank, http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB
2. Agency for toxic substances and disease Registry, http://www.atsdr.cdc.gov
3. NA: not available
4. The Extension Toxicology Network, http://extoxnet.orst.edu/

Compound	Phenol	
CAS	108-95-2	
Aerobic Degradation	Available data indicate that phenol biodegrades in soil under both aerobic and anaerobic soil conditions. The half-life of phenol in soil is generally <5 days (Baker and Mayfield, 1980), but acidic soils and some surface soils may have half-lives of up to 23 days (Shiu et al., 1994). Mineralization in an alkaline, parabrown soil under aerobic conditions was 45.5, 48, and 65% after 3, 7, and 70 days, respectively [1]	
Anaerobic Degradation	While degradation is slower under anaerobic conditions, evidence presented in the literature suggests that phenol can be rapidly and virtually completely degraded in soil under both aerobic and anaerobic conditions [1] Anaerobic degradation to carbon dioxide or methane also occurs (IPCS, 1994).	
Photolysis Degradation	Phenol does not absorb light in the region of 290–330 nm (Lide and Milne 1994); therefore, it should not photodegrade directly in the atmosphere.[1] Although phenol does not absorb light at wavelengths >290 nm, phenols react rapidly to sunlit natural water via an indirect reaction with photochemically produced hydroxyl radicals and peroxyl radicals; typical half-lives for hydroxyl and peroxyl radical reactions are on the order of 100 and 19.2 hours of sunlight, respectively (Canonica et al., 1995; Mill and Mabey, 1985). These reactions require dissolved natural organic materials that function as photosensitizers (Canonica et al., 1995). The estimated halflife for the reaction of phenol with photochemically produced singlet oxygen in sunlit surface waters contaminated by humic substances is 83 days. [1]	
Hydrolysis	No hydrolytic degradation is to be expected due to the chemical structure of the substance[2].	
Chemical behavior	Kd	NA[2]
	Log Koc	1.21-1.96[1]
	Log Kow	1.46[1]
	H	0.022 Pa*m^3/ mol at 20ºC[2]
	pKa	10[1]

Notes:
1. Agency for toxic substances and disease Registry, http://www.atsdr.cdc.gov
2. European Union Risk Assessment Report Risk on phenol, 2006.
3. NA: not available

APPENDIX C
MODEL DEVELOPMENT

The hydrodynamic model and water quality were completed by DHI. The Plantation sub-model was extracted from the Broward County model, which included the surface and groundwater features as they have a direct hydraulic connection to the proposed discharge location, the East Holloway Canal. Boundary conditions for the model area were extracted from the Broward model results for all of the groundwater and the surface water boundaries in the Plantation sub-model. Three representative microconstituents (sulfamethoxazole, phenol, triclosan) were selected for the water quality model based on their properties in photodegradation, sorption, and biodegradation, as well as their detections as part of this project.

C.1. MIKE SHE/MIKE 11 HYDROLOGIC MODEL

The MIKE SHE/MIKE 11 model includes components that represent the important processes of the land phase of the hydrologic cycle. MIKE SHE/MIKE 11 can represent physical processes using a variety of numerical methods that range from conceptual sub-basin based lumped parameter approaches to physics-based, and spatially distributed approaches. Processes that can be simulated with MIKE SHE/MIKE 11 include rainfall, evapotranspiration (ET), overland flow, channel flow and hydraulic routing, infiltration, unsaturated zone flow, irrigation, and groundwater flow. The processes that can be simulated with MIKE SHE/MIKE 11 are conceptually shown in Figure C.1.

Because the important land-based hydrologic and hydraulic processes can be represented with MIKE SHE/MIKE 11, it can be used as a planning and management tool to address a wide range of water resources and environmental problems.

In addition, MIKE SHE/MIKE 11 includes comprehensive advective-dispersive (AD) transport modules that were used in this project to evaluate the movement of microconstituents in the surface and groundwater. The MIKE SHE and MIKE 11 AD models are fully coupled and are capable of simulating bi-directional mass transfers between the groundwater and surface water components in addition to transport within individual components.

DHI incorporated the appropriate algorithms in the water quality model (ECO Lab) coupled with MIKE 11 to simulate the fate and transport of the selected microconstituents in the canals and rivers. The fate and transport of microconstituents in the overland, unsaturated, and saturated zone can be simulated in the groundwater and surface water bodies with MIKE SHE using process descriptions of varying complexity.

The MIKE SHE fate and transport modules allow conservative and simple reactive processes to be simulated, including:

- **Advection/Dispersion** - basic advection/dispersion solute transport module
- **Sorption/Degradation** - equilibrium/non-equilibrium adsorption and first-order degradation
- **Biodegradation** - advanced biological degradation

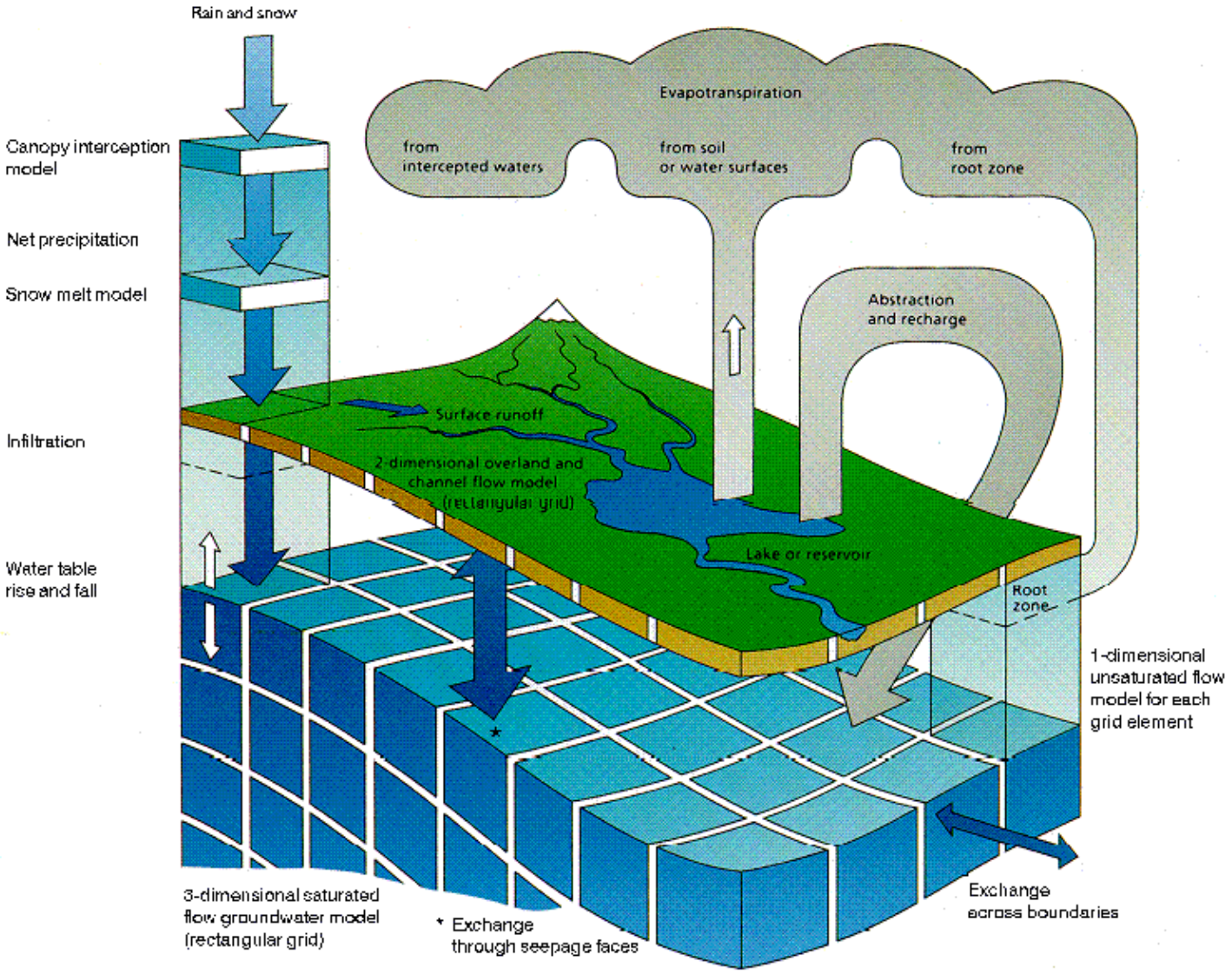


Figure C.1.Land-based hydrologic and hydraulic processes simulated with MIKE SHE/MIKE 11.

C.2. HYDRODYNAMIC MODEL

The Plantation hydrodynamic model maintains the same approach as the Broward County model. The MIKE SHE hydrologic model uses a 500-foot cell discretization, which pertains to the topography, the land use based and soil based parameters, and the hydrogeologic properties. The MIKE 11 hydraulic model includes the primary and secondary canals and main hydraulic structures (weirs, culverts, pumps and gates) for these canals. The urban tertiary system is conceptually represented in both the MIKE SHE and MIKE 11 models, as explained below.

In the Broward model, each Water Control District (WCD) sub-basin is represented as a runoff/drainage unit, where a certain control elevation and a common drainage outlet(s) are defined. The sub-basin outlets are typically the secondary canals located within the sub-basin controlled by structures that maintain the control elevation for the basin. In the absence of a secondary system, the runoff and subsurface drainage for the sub-basin is routed directly to the primary canals. Within the sub-basin, runoff, evapotranspiration, infiltration, irrigation, groundwater pumpage, and groundwater flow are simulated for every 500-foot cell in the sub-basin. The forces that drive these processes depend on the topographic gradients, the land use based and soil based parameters, and the hydrogeologic properties defined for each cell of the model.

In order to better handle the runoff of urban areas in the Broward model, the MIKE SHE Paved Area Runoff Module is used, instead of the Overland Flow Module. Each sub-basin is spatially represented in MIKE SHE by using a surface water routing map that assigns a routing code for each grid cell in a WCD sub-basin. Areas that are hydraulically connected are represented through the use of the same routing code value. A land use based runoff coefficient is specified for each grid cell. The runoff coefficient is a fractional value that indicates the fraction of water on the overland flow plane that is routed directly as paved area runoff to areas defined by the specified surface water routing map. In general, the paved area runoff coefficients increase as the degree of urbanization increases.

Rainfall that falls on each WCD sub-basin can move to a secondary or primary canal based on the water level gradient and the specified runoff coefficient. The water that does not leave the sub-basin via a MIKE 11 canal is available for evapotranspiration, infiltration, and groundwater pumpage and flow after infiltration. Outflow from a WCD sub-basin to a primary canal system is controlled using either a pump(s) or, if the sub-basin is connected by gravity, a conceptual fixed weir to maintain water levels in the sub-basin at the defined control elevations. For sub-basins controlled by a pump, the actual pump capacity is used in the model. For sub-basins with gravity connections to the secondary system, the drainage criterion, where known, was used to develop the maximum drainage rate for the sub-basin. Figure C.2 illustrates the exchange of flows in the MIKE SHE/MIKE 11 model. All significant primary and secondary canals in the Broward model area are represented in MIKE 11 using a level of detail sufficient to accurately simulate the dynamics of the primary and secondary canal system. The surface water routing map discussed above is used to route runoff from each grid cell to a defined location in the canal system simulated using MIKE 11.

In addition to the dynamics of the secondary system described above, there are components of the tertiary system such as swales, ditches, and exfiltration trenches that have connection to the groundwater and to the secondary canals. These features are conceptually represented in MIKE SHE using the drainage option. The same surface water routing map used for the paved area runoff module is used to route the drainage water. If the groundwater level

exceeds the specified drainage level it is then directly routed to the MIKE 11 canals at a specified drainage rate. This rate is function of the height of the groundwater above the drainage level and a calculated drainage conductance developed from a specified leakage coefficient for a cell and the cell area. In the Broward model, the drainage level has been set based on the control elevation for each WCD sub-basin.

Although internal basin storage is well represented as a result of using topographic data derived from Broward County's LIDAR data, the model also accounts for all significant storage, such as sub-division lakes, present in the interconnected surface water system in each WCD sub-basin. The internal surface water storage capacity of a sub-basin is physically represented in the topographic data used by MIKE SHE and conceptually in MIKE 11.

Internal sub-basin surface water storage is conceptually represented in MIKE 11 using a conceptual surface water storage node branch that contains all the surface water storage volume capacity in a sub-basin (*i.e.,* the total volume of all the lakes that are connected to the secondary drainage system in a sub-basin). In general, there is a MIKE 11 surface water storage node for each WCD sub-basin and each of these surface water storage nodes are appropriately connected to a secondary canal branch in that particular sub-basin. To control discharge from the surface water storage nodes to the secondary canal network, a conceptual weir has been defined at the outlet point. The weir crest elevation for each surface water storage node is based on the WCD sub-basin control elevation.

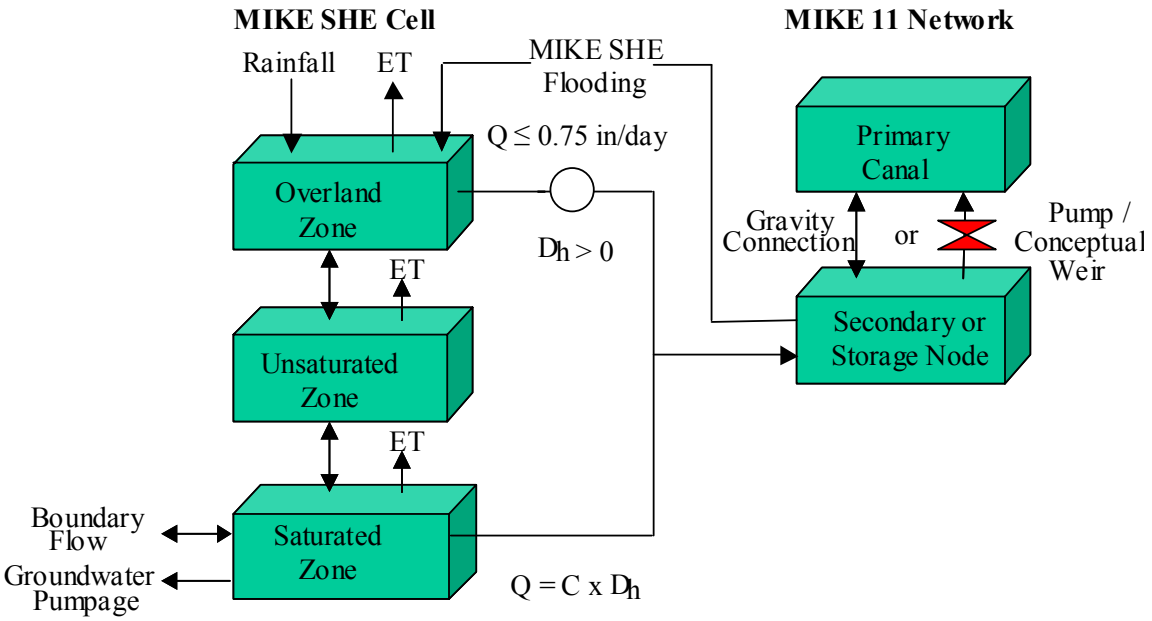


Figure C.2.Conceptualization of interaction between MIKE SHE and MIKE 11 for individual cells in a WCD sub-basin.

Water contained in the MIKE 11 surface water storage nodes is spatially distributed in MIKE SHE using the area inundation option (*i.e.,* flood codes). Use of flood codes allows MIKE SHE to map water simulated in MIKE 11 to the landscape based on simulated MIKE 11 stages and model topography. This mapping allows groundwater seepage and evapotranspiration to be spatially represented in a realistic way. To ensure realistic results

the total area defined with flood codes in a sub-basin corresponds to the area simulated in the MIKE 11 surface water storage node (Figure C.3).

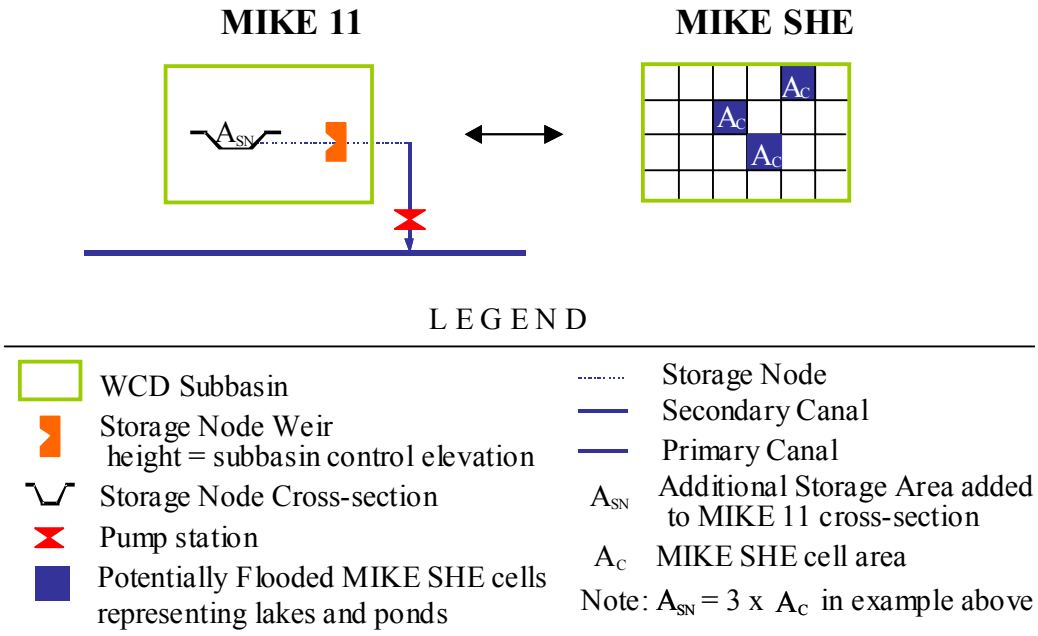


Figure C.3. Conceptualization of WCD storage nodes in MIKE 11 and MIKE SHE.

For WCD basins with surface water storage nodes, all paved area runoff for the sub-basin is routed to the surface water storage node to ensure that the dynamics of stage storage relationships are accurately simulated. In addition, a lake may receive sub-surface inflows from surrounding areas, which contribute to the water level in the storage node. MIKE SHE accounts for the ET in the storage nodes for all lakes where the MIKE 11 storage node water level exceeds the bottom elevation of the lake.

The focus of the modeling effort for this report is to trace the hypothetical wastewater effluent discharge to the Holloway Canal on the nearby surface and groundwater system, thus the Plantation sub-model extracted from the Broward County model includes only the surface and groundwater features that would have a direct hydraulic connection to the Holloway Canal. For the initial phase of the project, the spatial resolution was left the same as the Broward model (500-ft cell size). In later phases of the project the model can be refined to represent the area more accurately if necessary.

The model area was determined taking into account both the surface water basin divides and the groundwater capture areas. The model area and key features are shown on Figure C.4. The primary surface water basins included in the model are the C-12 and the eastern North New River Basins. The eastern North New River basin is defined by the areas east of the C-42 canal, which include the Old Plantation Water Control District (OPWCD) and the area east of the G-54 gates. The western sub-basins (Plantation Acres ID sub-basin and the areas west of it) were considered to be hydraulically disconnected and were excluded. The entire C-12 basin is included in the model area, but the secondary canals north of the C-12 canal were not included. Flows into and out of the C-12 canal from these secondary canals were taken from the Broward County Model results and are represented as boundary conditions.

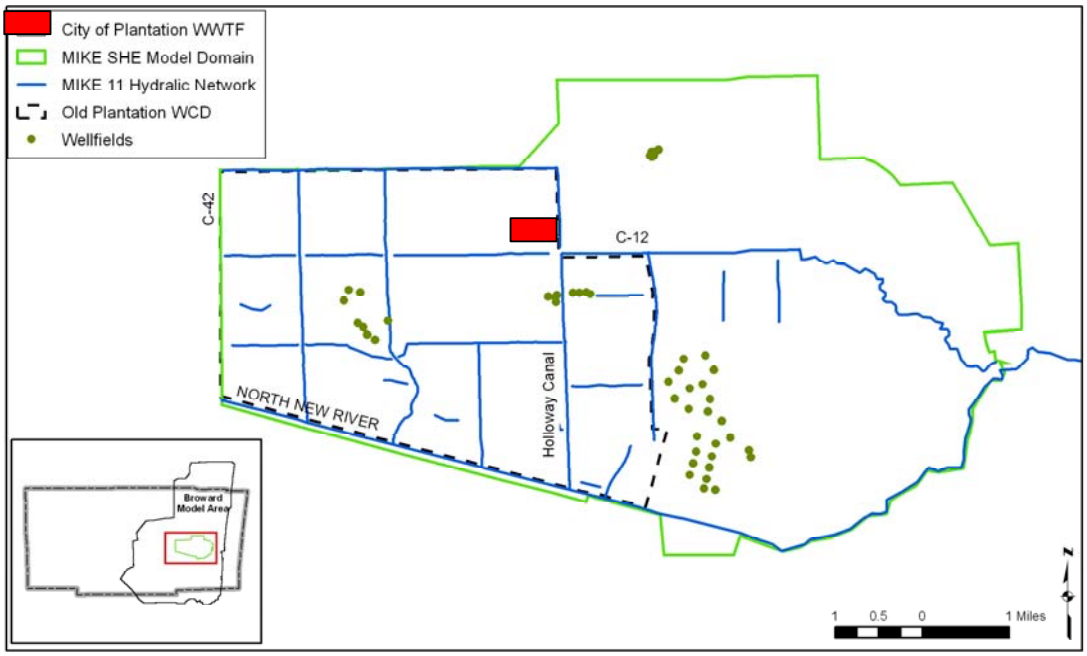


Figure C.4. Plantation model domain, river network and wellfield locations.

In addition, a preliminary study of the ground age was performed to determine the capture zone of the wellfields in the vicinity of the Holloway Canal by running a simple advection-dispersion transport model for the Broward model. For this simulation, a conservative tracer and a decaying tracer were used. The groundwater age was estimated using the following equation (Delhez et al., 2003),

$$T = (-\frac{1}{k})\ln(\frac{C_{decay}}{C_{conservative}})$$

Where,

K is the 1st order decay rate

C_{decay} is the concentration of the decaying tracer

$C_{conservative}$ is the concentration of the conservative tracer

The results show groundwater ages ranging from 1 to 10 years in the urban areas of the County. A groundwater capture zone for the wellfields in the proximity of the Holloway Canal was delineated from the differences in age. This area is shown on Figure C.5.

Boundary conditions for the model area were extracted from the Broward model results for all of the groundwater and the surface water boundaries in the Plantation sub-model. The northwest surface water boundary is the connection between the C-42 canal and the 3L3W secondary canal in the OPWCD. The southwest surface water boundary is the North New River just upstream of Canal No. 3. Both of these boundaries were set as water level boundaries. The eastern surface water boundary is the S-33 gates tailwater tidal signal.

The groundwater model for Broward County is composed of five hydrogeologic layers that represent the Surficial Aquifer system. All of these groundwater layers were also included in the Plantation sub-model. For each groundwater layer, the head elevation results from the Broward model were extracted and used as time varying and spatially distributed boundaries all along the outer boundary of the Plantation sub-model.

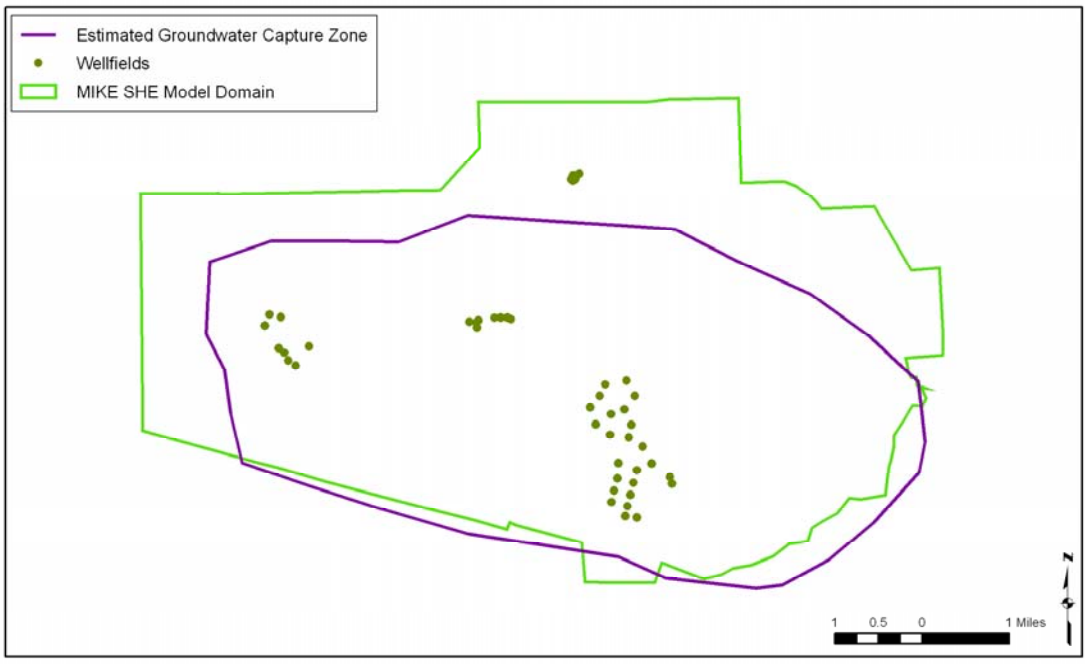


Figure C.5. Estimated groundwater capture area.

C.3. WATER QUALITY MODEL

In this section, the parameters introduced in the water quality model (fate and transport) are presented as well as their literature sources and the assumptions involved. The ECO Lab related parameters are described first followed by the ones used in MIKE SHE AD and MIKE11 AD modules. Finally, a description of the simulation is also included.

The MIKE 11 Water Quality module is known as ECO Lab. ECO Lab is integrated with the AD module of MIKE 11 and works dynamically with the hydrodynamic computations of MIKE SHE to simulate the fate and transport of water quality and biological constituents in the stream network. ECO Lab can handle a wide range of water quality processes ranging from simple first order decay to fully dynamic eutrophication processes. ECO Lab also has several standard templates of pre-defined ecosystem descriptions ready to be used for ecological modeling or serve as a starting point for more customized modeling.

A modification of the ECO Lab template designed for microconstituents was used to model the water quality processes for the Plantation Model (DHI, 2008c). The constants used in the template for each species are listed on Table C.1 and the source of the parameters and other assumptions are described next. The description is divided according to the processes where the parameters are involved. In general, when a range of parameters was reported, the more conservative limit was selected. In other words, the parameters that would cause the least degradation of the microconstituents were used in the model.

Table C.1. Input parameters assumed in the ECO LAB template

no	Description	Units	SM	TS	IB	4NP	MP	PH
1	Organic-carbon partitioning coefficient	l/kg	1585	19953	398	63096	501	251
2	Desorption rate in water	1/day				1		

no	Description	Units	SM	TS	IB	4NP	MP	PH
3	Desorption rate in sediment	1/day	0.1	0.02	0.1	0.01	0.1	0.1
4	Fraction of organic carbon in suspended solids SS	---	0.328					
5	Fraction of organic carbon in sediment	---	0.328					
6	Thickness of water film	Mm	0.1					
7	Ratio between thickness of diffusion layer in sediment and sediment thickness	---	0.5					
8	Factor for diffusion due to bioturbation, convection, etc.	---	10000					
9	Moleweight of the microconstituent molecule	g/mole	253.3	287.5	206.3	220.4	263.2	94.1
10	ECO Lab time step Controlled by MIKE11	S	120					
11	Density of dry sediment	kg/m^3 bulk	334.5					
12	Porosity of sediment	m^3 H_20 / m^3 bulk	0.83					
13	Settling velocity of SS	m/day	18.6					
14	Particle production rate	gdw/m^2/day	1.37					
15	Resuspension rate at velocities below or equal to ucrit	gdw/m^2/day	3.42					
16	Critical current velocity for sediment resuspension	m/s	0					
17	Factor for the resuspension rate term that is proportional to the water speed (above ucrit)	gdw/m^2/day*s/m	3330					
18	Minimum value for X_{SED}. Below, resuspension = 0	gdw/m^2	16725					
19	Biodecay rate water, max	1/day	0	0	0	0	0	0.14
20	Biodecay rate sediment, max	1/day	0	0	0	0	0	0.14
21	Halfsaturation constant biodecay water	gXE/ m^3	10^{-9}					
22	Halfsaturation constant biodecay sediment	gXE/ m^2	10^{-9}					
23	Arrhenius temperature coefficient for biodegradation	-	1					
24	Background concentration air	gXE/ m^3	0					
25	Light attenuation water column	1/m	2					
26	Photolysis rate at surface	1/day	2.52	0.07	0.00	1.11	0.09	0.01
27	Henry's constant	Pa m^3 / (mol K)	$9.69*10^{-8}$	$5.06*10^{-4}$	$1.54*10^{-2}$	3.45	$1.70*10^{-2}$	$3.37*10^{-2}$
28	Is the compound an acid [0/1]	-	0					
29	Is the compound a base [0/1]	-	0					
30	Dissociation constant acid ['pH units']	-	10					
31	Dissociation constant base ['pOH-units']	-	3					
32	Hydrolysis constant, acid	10^{-3}/day	0	0	0	0	7.79	0
33	Hydrolysis constant, neutral	10^{-3}/day	0	0	0	0	7.79	0
34	Hydrolysis constant, alkaline	10^{-3}/day	0	0	0	0	7.79	0
35	Universal gas constant	m^3 air Pa/ (mole*K)	8.3144					

Notes
SM: sulfamethoxazole, TS: triclosan, IB: ibuprofen, 4NP: 4 nonyl-phenol, MP: methyl parathion, PH: Phenol.

C.3.1. Adsorption on to soil particles (Table C.1, No. 1-5)

Adsorption and desorption of the dissolved species is considered in the microconstituents template for suspended and deposited sediment particles. The six examined microconstituents are mostly bound to the organic fraction (DHI, 2008c) and the corresponding partition coefficient in equilibrium is available from EPI suite software (EPA, 2008). The equilibrium between dissolved and adsorbed species is reached according to the desorption rates assumed in Table C.1, which is considered higher in open water than in sediment. Preliminary tests shown that in the cases with higher adsorption coefficient, desorption rates in the sediment layer must be set even lower in order to avoid numerical oscillations in the pore water concentration.

C.3.2. Diffusive transport at sediment-water interface (Table C.1, No. 6-9)

The transport of the dissolved species between the sediment and the open water layer is modeled in the microconstituent template as a diffusive process. The sediment layer depth is assumed initially as 20 cm and a thickness of water film much lower than that value would not affect the diffusive flux. On the other hand, the diffusion layer thickness in the sediment layer is assumed to be the half of the layer thickness.

The diffusion coefficient for the microconstituents molecules in water is found in the template from their molecular weights. The factor for diffusion due to bioturbation, vertical convection, etc. relates the effective diffusion coefficient with the molecular diffusion one. The effective diffusioncoefficient may be four orders of magnitude higher (Harvey et al., 2005; Langevin, 2001).

C.3.3. Sediment transport (Table C.1, No. 11-18)

The microconstituents template includes the mass of suspended solids (X_{SS}) and mass of sediment (X_{SED}) as variables. The mass balance of those variables involves the following processes: production of suspended particles, resuspension (or erosion) and settling (or deposition).

The original template (DHI, 2008c) considers a constant settling velocity and rate of resuspension, which are applied if the current water speed is lower and higher than a critical value, respectively. This approach was improved considering that deposition always occurs and that resuspension above a critical speed (ucrit) increases linearly with the current speed (cspd) as shown in the following equation:

$$\text{ressa} = \begin{cases} \text{resrat} & \text{cspd} \le \text{ucrit} \\ \text{resrat} + \text{fresrat}\,(\text{cspd} - \text{ucrit}) & \text{cspd} > \text{ucrit} \end{cases}$$

Where ressa is the resuspension rate per unit area, resrat is its value below ucrit, and fresrat is the factor to account for the speed dependency above ucrit.

A more complex treatment of the erosion-deposition terms can ben found in Tsujimoto (1999) and Xu et al. (2005).

Since there is no measured data available to calibrate the transport of suspended sediments in the canals; the model uses parameters from measurements conducted in the Water Conservation Areas (WCAs) and the Everglades in South Florida. The density of the dry sediment (or bulk density) and the organic matter mass fraction presented in Table C.1 were

estimated from the median value of the measurements conducted in the WCAs canals by Diaz et al. (2006). Grain densities of 2.56 g/cm^3 for inorganic and 1.288 g/cm^3 for organic matter were found from the measurements on suspended particles in the Everglades reported by Bazante et al. (2006). The porosity of the sediment layer was computed from these values as:

$$\text{porosity} = 1 \text{ bulk density} / \text{average grain density}.$$

The settling velocity of the suspended particles was estimated as the quotient between the average deposition rate and the average concentration. The values for average deposition rate and the average concentration reported for the Everglades marsh were 12.3 gdw/m^2/d by Leonard et al. (2006) and 1 mg/l by Bazante et al. (2006), respectively. The particle production rate is assumed as a typical leaf litter production rate in Everglades marsh areas adopted from the range reported by Ewe et al. (2006).

The resuspension rate was estimated from the deposition rates measured at different velocities by Leonard et al. (2006) at the Everglades marsh. In equilibrium the deposition rate is equal to the production plus the resuspension rates. The deposition rates measured by Leonard et al. (2006) increases with typical water speeds at the measurement points, following approximately a linear dependence in the speed range reported (0 to 1 cm/s). The linear fitting of this dependence gives the parameters No. 15 and 17 in Table C.1. Moreover, the critical velocity for sediment resuspension was assumed to be zero, which is in accordance to other resuspension processes different from erosion, such as gas production in the sediment layer and thermal convective movement in the water column. Finally, after model testing, it was determined that the minimum value for X_{SED} necessary to assure numerical stability (parameter No. 18) is 16725 gdw/m^2, which is equivalent to a 5-cm thick sediment layer.

C.3.4. Biodegradation (Table C.1, No. 19-23)

According to the EPI suite software (EPA, 2008), Phenol is the only microconstituent from the six included in the literature review that is reported as biodegradable in all the literature sources. In general, the biodegradation rates depend on local conditions and the reported values cover a wide range.

As shown in Table C.1, the model assumes the most conservative case for biodegradation. The biodecay rate is then considered to be zero for all the species, except for phenol where the maximum half-life reported (120 hours) is used. The dependency of the phenol biodecay rate on concentration and temperature was unknown and therefore not considered.

C.3.5. Photolysis (Table C.1, No. 25-26)

The photolysis decay rate at the surface was also assumed conservatively and set to the lowest value from the range reported in the literature review. The light attenuation in water column is used in the template to translate the decay rate at the surface to the whole water column. The minimum value for the attenuation coefficient is measured in pure water and it is around 0.15 m^{-1} (Gallegos and Kenworthy, 1996). The conservative value presented on Table 1 (2 m^{-1}) was reported by (McPherson and Miller, 1987) for Charlotte Harbor, FL.

C.3.6. Evaporation (Table C.1, No. 24, 27-31)

The microconstituents ECO lab template computes the evaporation rate of the dissolved species by using the Henry's constant, which was obtained from EPI suite software (EPA, 2008) at 25^{o}C. A negligible background concentration in air was assumed. None of the compounds are assumed acids or bases; thus, no dissociation effects in the evaporation rate are considered in the model. The effect of the wind velocity on the evaporation rate is included in the model. For wind velocity, which is a forcing variable in the template, a constant value of 1.5 m/s (a typical value for the area) was assumed.

C.3.7. Hydrolysis (Table C.1, No. 32-35)

Methylparathion is the only microconstituent in the Literature Review that is reported degradable by hydrolysis. This contaminant is not among the three simulated in the water quality model and therefore, degradation by hydrolysis is not included in this study. The decay rate shown in Table C.1 was estimated conservatively from the range reported in the literature review. The dependence of this rate on the PH is not well known and therefore not considered by the tabulated parameters.

C.4. ADVECTION-DISPERSION TRANSPORT MODEL

The ECO lab template computes all the water quality processes described in the previous section in the surface water (MIKE11) network. The transport vehicle for the movement of contaminants in MIKE 11 is the Advection-Dispersion (AD) module. The MIKE 11 AD can exchange solute transport with the AD module in MIKE SHE, which in turn can exchange solute transport in all its modules: overland flow, evapotranspiration (plant uptake), unsaturated zone, and saturated zone. The contaminant transport pathway of interest in the Plantation Model begins at the WWTP point source discharge at the Holloway Canal throughout the connecting canals and ultimately into the wellfields. Thus, the solute transport interaction between the canals in MIKE 11 and in the saturated zone in MIKE SHE is the most important. The overland flow AD is also included in the model because it is a requirement in MIKE SHE if MIKE 11 AD is linked. Transport through the unsaturated zone or plant uptake was not considered a significant pathway for the purposes of this study and can considerably increase model running time; thus, have been excluded from the model.

MIKE SHE considers adsorption and decomposition processes in saturated zone layers and in overland layer. However, it does not include the transport of suspended particles in the overland flow module and the corresponding adsorbed microconstituents. The saturated zone (SZ) module considers groundwater abstractions from wells and drainage to the MIKE 11 canals as sinks, where the concentration is equal to the actual solute concentration in the SZ grids.

In order to solve the advection-dispersion equation, the model requires initial and boundary conditions, and dispersion coefficients. The values used for the MIKE SHE and MIKE 11 AD transport model parameters are described below.

C.4.1. Initial conditions

The background concentrations of the different microconstituents in the model area are likely very low. Thus, the model is assumed to have zero concentration of microconstituents at the beginning of the simulation, which is a conservative assumption. The initial mass for the overland flow component is set uniformly as 0 g/m^2. And the initial concentration is set to 0 g/m^3 in both, the ground water layers in MIKE SHE and at the canal network in MIKE11.

C.4.2. Boundary conditions

For the canal network, all the boundary conditions for the dissolved and adsorbed microconstituents are assumed to have zero concentration, which means no external mass input. The only source of the microconstituents in the model is in the discharge coming out from the WWTP. The concentrations specified at the WWTP are shown in Table C.2. Those values are based on selected results from this project. The concentration of suspended particles is assumed to be 1 mg/l at all the open boundaries of the canal network. This value corresponds to the equilibrium concentration when water speed is around 0.4 cm/s (0.013 ft/s).

The concentrations of the dissolved microconstituent in overland and groundwater boundaries were set to zero. In the Plantation model, the concentration in the rainfall is also assumed to be zero and no plant uptake is considered. Pumping wells and drainage features extract mass from the saturated zone component at the existing groundwater concentration.

C.4.3. Dispersion coefficient

The dispersion coefficient for the overland flow layer in MIKE SHE is assumed to be isotropic. A value of 5 m^2/s is used in the model, which is a typical value according to the MIKE11 user manual (DHI, 2008b). In MIKE SHE the dispersion coefficient is considered proportional to the velocity in the groundwater layers. The longitudinal and transversal dispersivity coefficients are set equal to 5 m and 0.5 m, respectively, which are typical ranges reported by Langevin (2001). For the canal network in MIKE11, the dispersivity coefficient and the maximum dispersion coefficient are assumed to be 5 m and 5 m^2/s, respectively.

C.4.4. Adsorption processes

MIKE SHE considers the adsorption processes in SZ layers. In this model, a bulk density of 2000 kg/m^3, a porosity of 0.2 and an organic fraction of 0.05 are assumed for all five groundwater layers. The organic-carbon partitioning coefficients from Table 1 are also used for groundwater adsorption. These values were converted to the MIKE SHE input units (l/kg = 10^{-6} m^3/g).

C.4.5. Decay processes

The decay processes in MIKE SHE are represented using a simpler approach than ECO Lab. In the overland layer, a total decay rate for each microconstituent is estimated from the sum of the biodegradation, photolysis, hydrolysis and evaporation rates estimated under certain conditions, which are shown in Table C.2. Decay in the SZ layers is assumed to occur only by hydrolysis. However, none of the microconstituents included in the model degrade by hydrolysis; thus, they do not undergo decay in the groundwater. The decay rates in Table 15 are converted to half life time ($t_{1/2}$), which is the parameter input in MIKE SHE.

Table C.2. Input parameters for Advection-Dispersion transport model

Description	units	CT	SM	TS	IB	4NP	MP	PH
Concentration in water coming from WWTP	ng/l	100	76	5	2.7	25	25	100
Biodecay rate	1/day	0	0	0	0	0	0	0.14
Photolysis rate at surface	1/day	0	2.52	0.07	0.00	1.11	0.09	0.01
Hydrolysis rate	1/day	0	0	0	0	0	0.00779	0

Description	units	CT	SM	TS	IB	4NP	MP	PH
Evaporation lost rate (at 1m/s wind speed, 1m water depth)	1/day	0	0.00	0.06	0.21	0.22	0.20	0.27
Total decay rate OL (All four processes)	1/day	0	2.52	0.13	0.21	1.33	0.29	0.42
	1/h	0	0.105	0.005	0.008	0.055	0.012	0.017
Half-life ($t_{1/2}$) in OL (All four processes)	10^{-3} year	10^{9}	0.753	14.6	9.14	1.43	6.56	4.55
Total decay rate GW (only hydrolysis)	1/day	0	0	0	0	0	0.00779	0
Half-life ($t_{1/2}$) in GW	years	10^{6}	10^{6}	10^{6}	10^{6}	10^{6}	0.244	10^{6}

C.5. SIMULATION DESCRIPTION

C.5.1. Hydrodynamic model

The Plantation sub-model, extracted from the Broward County model, includes only the surface and groundwater features that would have a direct hydraulic connection to the Holloway Canal. For this initial phase of the project, the spatial resolution remains the same as the Broward model (500-ft cell size). In later phases of the project, the model can be refined to represent the area more accurately if necessary.

The model area was determined considering the surface water basin divides and the groundwater capture areas. The primary surface water basins included in the model are the C-12 and the eastern North New River Basins. The eastern North New River basin is defined by the areas east of the C-42 canal, which include the Old Plantation Water Control District (OPWCD) and the area east of the G-54 gates. The western sub-basins (Plantation Acres ID sub-basin and the areas west of it) were considered to be hydraulically disconnected and were excluded. The entire C-12 basin is included in the model area, but the secondary canals north of the C-12 canal were not included. Flows into and out of the C-12 canal from these secondary canals were taken from the Broward County Model results are represented as boundary conditions.

The hydrodynamic model is run for a four-year period (1/1/1999 to 12/31/2002); which corresponds to the Broward County Model calibration (1/1/1999 - 12/31/2000) and verification (1/1/2001 - 12/31/2002) periods. This period includes one wet year, including a hurricane event, (1999), one dry year (2000), and two average years (2001-2002). The river network and the surface topography are shown in Figure C.6 and Figure C.7, respectively.

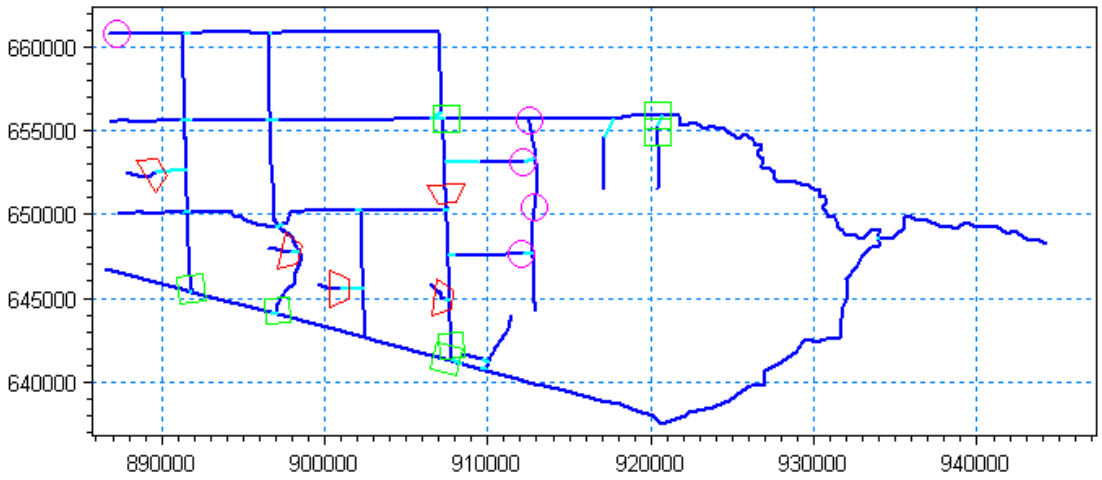


Figure C.6.River network and structures in the Plantation Model. Blue lines represent branches, cyan lines are branches connectors, red trapezoids are weirs, purple circles are culverts and green squares control structures.

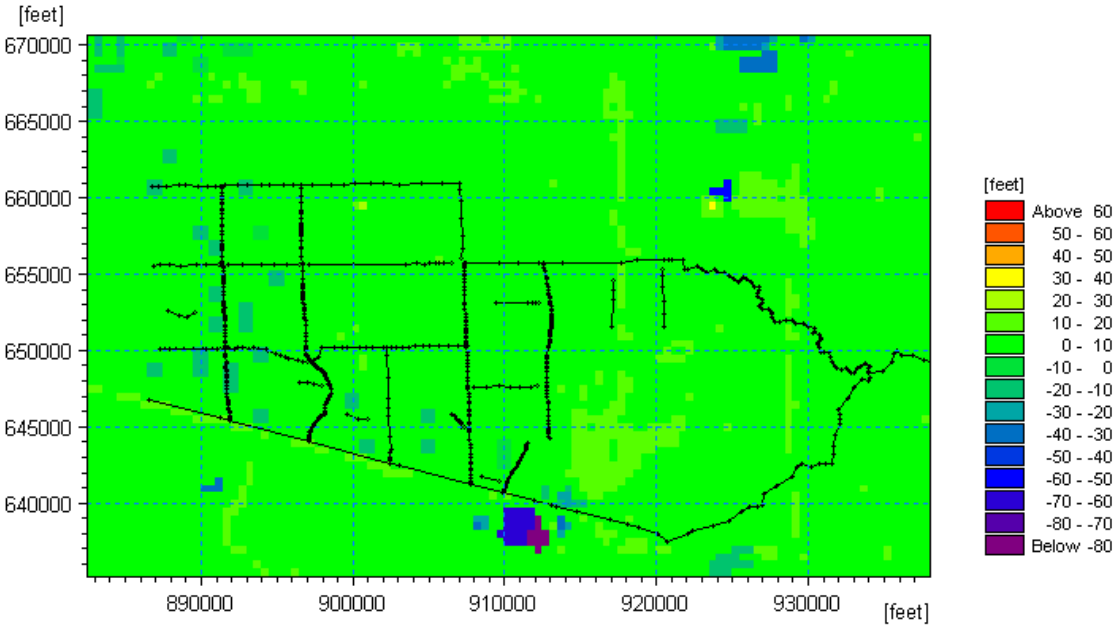


Figure C.7. Model topography (ft NGVD 29).

C.5.2. Water quality model

Preliminary water quality model runs for the four-year period show that the concentration of the microconstituents in groundwater at the potable-water wellfield locations does not reach steady concentration levels when starting from a zero-concentration model. Thus, the water quality simulation period was extended to 20 years in order to see the maximum concentrations in ground water at wellfield locations at the end of that period. The simulation period was extended by concatenating five times all the 4-year data from the hydrodynamic model. In other words, the hydrologic information for the period of 1999 through 2002 is repeated 5 times.

Separate water quality models were built for each of the three selected microconstituents: sulfamethoxazole (SM), triclosan (TS) and phenol (PH), and for the conservative tracer (CT). The objective of the water quality model is to study the transport of microconstituents that exhibit different removal/retention mechanisms: adsorption, biodegradation, photolysis and evaporation. Thus, the selection of the microconstituents for the model was mainly based on their possible degradation pathways. Also the concentrations detected during the chemical analysis at different stages of the WWTP were considered.

Triclosan and phenol have very high and very low adsorption coefficients in soil, respectively. Phenol is the only microconstituent, of the six in the Literature Review, that biodegrades and it has the highest evaporation rate. Sulfamethoxazole is the microconstituent with highest photolysis decomposition rate. The effect of those processes (adsorption, biodegradation, photolysis and evaporation) can be observed by comparing the results for the three microconstituents and the conservative tracer.

REFERENCES

Ahel, M., Scully, F. E., Hoigné, J., and Giger, W. (1994). "Photochemical degradation of nonylphenol and nonylphenol polyethoxylates in natural waters." *Chemosphere*, 28(7), 1361-1368.

Alum, A., Yoon, Y., Westerhoff, P., and Abbaszadegan, M. (2004). "Oxidation of bisphenol A, 17beta-estradiol, and 17alpha-ethynyl estradiol and byproduct estrogenicity." *Environ Toxicol*, 19(3), 257-264.

Anderson, P. D. (2005). "Technical brief: Endocrine disrupting compounds and implications for wastewater treatment." *WERF 04-WEM-6*, Water Environment Research Foundation, Alexandria, Virginia.

ATSDR. (2008). "The Agency for Toxic Substances and Disease Registry." <http://www.atsdr.cdc.gov>.

Auriol, M., Filali-Meknassi, Y., Adams, C. D., and Tyagi, R. D. (2006). "Natural and synthetic hormone removal using the horseradish peroxidase enzyme: temperature and pH effects." *Water research*, 40(15), 2847-2856.

Auriol, M., Filali-Meknassi, Y., Adams, C. D., Tyagi, R. D., Noguerol, T. N., and Pina, B. (2008). "Removal of estrogenic activity of natural and synthetic hormones from a municipal wastewater: efficiency of horseradish peroxidase and laccase from Trametes versicolor." *Chemosphere*, 70(3), 445-452.

Badawy, M. I., and el-Dib, M. A. (1984). "Persistence and fate of methyl parathion in sea water." *Bull Environ Contam Toxicol*, 33(1), 40-49.

Baker, M., and Mayfield, C. (1980). "Microbial and non-biological decomposition of chlorophenols and phenol in soil." *Water, Air, & Soil Pollution*, 13(4), 411-424.

Barber, L. B., Furlong, E. T., Keefe, S. H., Brown, G. K., and Cahill, J. D. (2000). "Natural and contaminant organic compounds in the boulder creek watershed, Colorado during high-flow and low-flow conditions." *Water-Resources Investigations Report 03-4045*, USGS.

Barel-Cohen, K., Shore, L. S., Shemesh, M., Wenzel, A., Mueller, J., and Kronfeld-Schor, N. (2006). "Monitoring of natural and synthetic hormones in a polluted river." *Journal of environmental management*, 78(1), 16-23.

Barnes, K. K., Kolpin, D. W., Meyer, M. T., Thurman, E. M., Furlong, E. T., Zaugg, S. D., and Barber, L. B. (2002). "Water-quality data for pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999-2000." *Report 02-94*, USGS.

Baronti, C., Curini, R., D'Ascenzo, G., Di Corcia, A., Gentili, A., and Samperi, R. (2000). "Monitoring natural and synthetic estrogens at activated sludge sewage treatment plants and in a receiving river water." *Environ. Sci. Technol.*, 34(24), 5059-5066.

Bazante, J., Jacobi, G., Solo-Gabriele, H. M., Reed, D., Mitchell-Bruker, S., Childers, D. L., Leonard, L., and Ross, M. (2006). "Hydrologic measurements and implications for tree island formation within Everglades National Park." *Journal of Hydrology*, 329(3-4), 606-619.

Bellona, C., and Drewes, J. E. (2007). "Viability of a low-pressure nanofilter in treating recycled water for water reuse applications: a pilot-scale study." *Water research*, 41(17), 3948-3958.

Bevans, H. E., Goodbred, S. L., Miesner, J. F., Watkins, S. A., Gross, T. S., Denslow, N. D., and Schoeb, T. (1996). "Synthetic organic compounds and carp endocrinology and histology in Las Vegas Wash and Las Vegas and Callville Bays of Lake Mead, Nevada, 1992 and 1995." *Water-Resources Investigations Report 96-4266*, United

States Geological Survey, Carson City, Nevada. <http://pubs.er.usgs.gov/pubs/wri/wri964266>.
Bila, D., Montalvao, A. F., Azevedo Dde, A., and Dezotti, M. (2007). "Estrogenic activity removal of 17beta-estradiol by ozonation and identification of by-products." *Chemosphere*, 69(5), 736-746.
Blazer, V. S., Iwanowicz, L. R., Iwanowicz, D. D., Smith, D. R., Young, J. A., Hedrick, J. D., Foster, S. W., and Reeser, S. J. (2007). "Intersex (*Testicular Oocytes*) in Smallmouth Bass from the Potomac River and Selected Nearby Drainages." *Journal of Aquatic Animal Health*, 19(4), 242-253.
Boyd, G. R., Palmeri, J. M., Zhang, S., and Grimm, D. A. (2004). "Pharmaceuticals and personal care products (PPCPs) and endocrine disrupting chemicals (EDCs) in stormwater canals and Bayou St. John in New Orleans, Louisiana, USA." *The Science of the total environment*, 333(1-3), 137-148.
Broward County. (2006). "Recalibration and consolidation of integrated surface water and groundwater models for Broward County." Broward County Environmental Protection Department Water Resources Division,, Broward County, Florida.
Brun, G. L., Bernier, M., Losier, R., Doe, K., Jackman, P., and Lee, H. B. (2006). "Pharmaceutically active compounds in atlantic canadian sewage treatment plant effluents and receiving waters, and potential for environmental effects as measured by acute and chronic aquatic toxicity." *Environmental toxicology and chemistry / SETAC*, 25(8), 2163-2176.
Camp Dresser & McKee Inc. (2002). "Modeling Water Management Practices in Central Broward County, Florida." Broward County Environmental Protection Department, Broward County, Florida.
Camp Dresser & McKee Inc. (2005a). "Modeling Water Management Practices in Northern Broward County, Florida." Broward County Environmental Protection Department, Broward County, Florida.
Camp Dresser & McKee Inc. (2005b). "South Area Drainage Assessment MIKE SHE Model Report." Broward County Environmental Protection Department, Broward County, Florida.
Canonica, S., Jans, U., Stemmler, K., and Hoigne, J. (1995). "Transformation kinetics of phenols in water: photosensitization by dissolved natural organic material and aromatic ketones." *Environ. Sci. Technol.*, 29(7), 1822-1831.
Canonica, S., Meunier, L., and von Gunten, U. (2008). "Phototransformation of selected pharmaceuticals during UV treatment of drinking water." *Water research*, 42(1-2), 121-128.
Carballa, M., Omil, F., and Lema, J. M. (2005). "Removal of cosmetic ingredients and pharmaceuticals in sewage primary treatment." *Water research*, 39(19), 4790-4796.
Cartinella, J. L., Cath, T. Y., Flynn, M. T., Miller, G. C., Hunter, K. W., Jr., and Childress, A. E. (2006). "Removal of natural steroid hormones from wastewater using membrane contactor processes." *Environmental science & technology*, 40(23), 7381-7386.
CDPH. (2008). "Groundwater Recharge Reuse Draft Regulations." California Department of Public Health, <http://www.cdph.ca.gov/healthinfo/environhealth/water/pages/waterrecycling.aspx> .
Chang, S., Jang, N., Yeo, Y., and Kim, I. S. (2006). "Fate and transport of endocrine-disrupting compounds (oestrone and 17beta-oestradiol) in a membrane bio-reactor used for water re-use." *Water Sci Technol*, 53(9), 123-130.
Clara, M., Strenn, B., Gans, O., Martinez, E., Kreuzinger, N., and Kroiss, H. (2005). "Removal of selected pharmaceuticals, fragrances and endocrine disrupting

compounds in a membrane bioreactor and conventional wastewater treatment plants." *Water research*, 39(19), 4797-4807.
Coors, A., Jones, P. D., Giesy, J. P., and Ratte, H. T. (2003). "Removal of estrogenic activity from municipal waste landfill leachate assessed with a bioassay based on reporter gene expression." *Environmental science & technology*, 37(15), 3430-3434.
Damstra, T., Barlow, S., Bergman, A., Kavlock, R., and Van der Kraak, G. (2002). "Global assessment of the state-of-the-science of endocrine disruptors." *WHO/PCS/EDC/02.2*, World Health Organization, International Programme on Chemical Safety Geneva, Switzerland.
Deborde, M., Rabouan, S., Duguet, J. P., and Legube, B. (2005). "Kinetics of aqueous ozone-induced oxidation of some endocrine disruptors." *Environmental science & technology*, 39(16), 6086-6092.
Delhez, É. J. M., Deleersnijder, É., Mouchet, A., and Beckers, J. M. (2003). "A note on the age of radioactive tracers." *Journal of Marine Systems*, 38(3-4), 277-286.
Denslow, N. D., Chow, M. C., Kroll, K. J., and Green, L. (1999). "Vitellogenin as a biomarker of exposure for estrogen or estrogen mimics." *Ecotoxicology*, 8(5), 385-398.
DHI. (2008a). "Broward County Integrated Water Resource Management Master Plan Task 1.3 - MIKE SHE/MIKE 11 Baseline Model Technical Memorandum." consultant report prepared fro Broward County.
DHI. (2008b). "A modelling system for Rivers and Channels. User Guide."
DHI. (2008c). "Xenobiotics template. ECO Lab. Scientific Description."
Diaz, O. A., Daroub, S. H., Stuck, J. D., Clark, M. W., Lang, T. A., and Reddy, K. R. (2006). "Sediment inventory and phosphorus fractions for water conservation area canals in the Everglades." *Soil Sci Soc Am J*, 70(3), 863-871.
Diniz, M. S., Peres, I., Magalhaes-Antoine, I., Falla, J., and Pihan, J. C. (2005). "Estrogenic effects in crucian carp (Carassius carassius) exposed to treated sewage effluent." *Ecotoxicology and environmental safety*, 62(3), 427-435.
Drewes, J. E., Hemming, J. D. C., Schauer, J. J., and Sonzogni, W. C. (2006a). "Removal of endocrine disrupting compounds in water reclamation processes." *WERF Report 01-HHE-20T*, Water Environment Research Foundation Report 01-HHE-20T, Alexandria, VA.
Drewes, J. E., Xu, P., Bellona, C., Oedekoven, M., Macalady, D., Amy, G., and Kim, T.-U. (2006b). "Rejection of wastewater-drived micropollutants in high-pressure membrane applications leading to indirect potable reuse." *WRF 02-001*, WaterReuse Foundation, Alexandria, VA.
Drillia, P., Dokianakis, S. N., Fountoulakis, M. S., Kornaros, M., Stamatelatou, K., and Lyberatos, G. (2005). "On the occasional biodegradation of pharmaceuticals in the activated sludge process: The example of the antibiotic Sulfamethoxazole." *Journal of Hazardous Materials*, 122, 259 - 265.
EPA-EDSP. (2008). "Endocrine Disruptor Screening Program." United States Environmental Protection Agency, Washington, DC. <http://www.epa.gov/endo/>.
EPA-EDSTAC. (1998). "Endocrine Disruptor Screening and Testing Advisory Committee (EDSTAC) Final Report." United States Environmental Protection Agency, Endocrine Disruptor Screening and Testing Advisory Committee, Washington, DC. <http://www.epa.gov/endo/pubs/edspoverview/finalrpt.htm>.
EPA. (1978). "Environmental pathways of selected chemicals in freshwater systems: Part II. Laboratory studies." *EPA-600/7-78/074.*, U.S. Environmental Protection Agency, Office of Research and Development, Environmental Research Laboratory, Athens, GA.

EPA. (1994). "Short term methods for estimating the chronic toxicity of effluents and receiving waters to freshwater organisms." *EPA 600/4-91/002.*, U.S. Environmental Protection Agency.
EPA. (2002). "Short term methods for estimating the chronic toxicity of effluents and receiving waters to freshwater organisms." *EPA-821-R-02-013*.
EPA. (2005). "Ambient Water Quality Criteria - Nonylphenol. Final. ." *EPA-822-R-05-005*, United States Environmental Protection Agency, Office of Water. <http://www.epa.gov/waterscience/criteria/nonylphenol/final-doc.pdf>.
EPA. (2007). "Draft list of initial pesticide active ingredients and pesticide inerts to be considered for screening under the Federal Food, Drug, and Cosmetic Act. ." Federal Register, 72(116), 33486-33503.
EPA. (2008). "EPI suite software version 3.20." < http://epa.gov/opptintr/exposure/pubs/episuite.htm>.
Ewe, S., L., M., Gaiser, E. E., Childers, D. L., Iwaniec, D., Rivera-Monroy, V. H., and Twilley, R. R. (2006). "Spatial and temporal patterns of aboveground net primary productivity (ANPP) along two freshwater-estuarine transects in the Florida Coastal Everglades." *Hydrobiologia*, 569, 459-474.
Falconer, I. R. (2006). "Are endocrine disrupting compounds a health risk in drinking water?" *International journal of environmental research and public health*, 3(2), 180-184.
Folmar, L. C., Denslow, N. D., Kroll, K., Orlando, E. F., Enblom, J., Marcino, J., Metcalfe, C., and Guillette, L. J., Jr. (2001). "Altered serum sex steroids and vitellogenin induction in walleye (Stizostedion vitreum) collected near a metropolitan sewage treatment plant." *Archives of environmental contamination and toxicology*, 40(3), 392-398.
Folmar, L. C., Denslow, N. D., Rao, V., Chow, M., Crain, D. A., Enblom, J., Marcino, J., and Guillette, L. J., Jr. (1996). "Vitellogenin induction and reduced serum testosterone concentrations in feral male carp (Cyprinus carpio) captured near a major metropolitan sewage treatment plant." *Environmental health perspectives*, 104(10), 1096-1101.
Fukuhara, T., Iwasaki, S., Kawashima, M., Shinohara, O., and Abe, I. (2006). "Absorbability of estrone and 17beta-estradiol in water onto activated carbon." *Water research*, 40(2), 241-248.
Gallegos, C. L., and Kenworthy, W. J. (1996). "Seagrass depth limits in the Indian river lagoon (Florida, U.S.A.): Application of an optical water quality model." *Estuarine, Coastal and Shelf Science*, 42, 267-288.
Gebhardt, W., and Schroder, H. F. (2007). "Liquid chromatography-(tandem) mass spectrometry for the follow-up of the elimination of persistent pharmaceuticals during wastewater treatment applying biological wastewater treatment and advanced oxidation." *Journal of chromatography*, 1160(1-2), 34-43.
Giesy, J. P., Snyder, E. M., Nichols, K. M., Snyder, S. A., Villalobos, S. A., Jones, P. D., and Fitzgerald, S. D. (2003). "Examination of reproductive endpoints in goldfish (Carassius auratus) exposed in situ to municipal sewage treatment plant effluent discharges in Michigan, USA." *Environmental toxicology and chemistry / SETAC*, 22(10), 2416-2431.
Göbel, A., McArdell, C. S., Joss, A., Siegrist, H., and Giger, W. (2007). "Fate of sulfonamides, macrolides, and trimethoprim in different wastewater treatment technologies." *Science of The Total Environment*, 372(2-3), 361-371.
Gomez, M. J., Martinez Bueno, M. J., Lacorte, S., Fernandez-Alba, A. R., and Aguera, A. (2007). "Pilot survey monitoring pharmaceuticals and related compounds in a sewage treatment plant located on the Mediterranean coast." *Chemosphere*, 66(6), 993-1002.

Graham, N., Jiang, C. C., Li, X. Z., Jiang, J. Q., and Ma, J. (2004). "The influence of pH on the degradation of phenol and chlorophenols by potassium ferrate." *Chemosphere*, 56(10), 949-956.
GWRC. (2003). "Endocrine disrupting compounds: knowledge gaps and research needs." Global Water Research Coalition, UK.
Hanselman, T. A., Graetz, D. A., and Wilkie, A. C. (2003). "Manure-borne estrogens as potential environmental contaminants: a review." *Environmental science & technology*, 37(24), 5471-5478.
Harvey, J. W., Saiers, J. E., and Newlin, J. T. (2005). "Solute transport and storage mechanisms in wetlands of the Everglades, south Florida, ." *Water Resour. Res.*, 41, W05009.
Hazen and Sawyer, P. C. (2007). "Technical mmorandum: advanced wastewater treatment pilot project."
Hemming, J. M., Allen, H. J., Thuesen, K. A., Turner, P. K., Waller, W. T., Lazorchak, J. M., Lattier, D., Chow, M., Denslow, N., and Venables, B. (2004). "Temporal and spatial variability in the estrogenicity of a municipal wastewater effluent." *Ecotoxicology and environmental safety*, 57(3), 303-310.
Hemming, J. M., Waller, W. T., Chow, M. C., Denslow, N. D., and Venables, B. (2001). "Assessment of the estrogenicity and toxicity of a domestic wastewater effluent flowing through a constructed wetland system using biomarkers in male fathead minnows (*Pimephales promelas* rafinesque, 1820)." *Environmental toxicology and chemistry / SETAC*, 20(10), 2268-2275.
HSDB. (2008). "Hazardous Substance Data Bank (HSDB)." <http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB>.
Hu, J. Y., Chen, X., Tao, G., and Kekred, K. (2007a). "Fate of endocrine disrupting compounds in membrane bioreactor systems." *Environmental science & technology*, 41(11), 4097-4102.
Hu, L., Gao, N. Y., Xu, B., Li, R. Y., Zhao, J. F., and Liu, S. Q. (2007b). "Mineralization of BPA by combination of UV/H_2O_2/micro-aeration process " *Huan Jing Ke Xue (in Chinese)*, 28(7), 1496-1501.
Hua, W., Bennett, E. R., and Letcher, R. J. (2006). "Ozone treatment and the depletion of detectable pharmaceuticals and atrazine herbicide in drinking water sourced from the upper Detroit River, Ontario, Canada." *Water research*, 40(12), 2259-2266.
Huber, M. M., Gobel, A., Joss, A., Hermann, N., Loffler, D., McArdell, C. S., Ried, A., Siegrist, H., Ternes, T. A., and von Gunten, U. (2005a). "Oxidation of pharmaceuticals during ozonation of municipal wastewater effluents: a pilot study." *Environmental science & technology*, 39(11), 4290-4299.
Huber, M. M., Korhonen, S., Ternes, T. A., and von Gunten, U. (2005b). "Oxidation of pharmaceuticals during water treatment with chlorine dioxide." *Water research*, 39(15), 3607-3617.
Huber, M. M., Ternes, T. A., and von Gunten, U. (2004). "Removal of estrogenic activity and formation of oxidation products during ozonation of 17alpha-ethinylestradiol." *Environmental science & technology*, 38(19), 5177-5186.
IEH. (2005). "Chemicals Purported to be Endocrine Disruptors: a Compilation of Published Lists." *Web Report W20*, Institute for Environment and Health, Leicester, United Kingdom. <http://www.silsoe.cranfield.ac.uk/ieh/pdf/w20.pdf>.
IPCS. (1994). "Phenol health and safety guide." *Health and Safety Guide No. 88*, World Health Organization for the International Programme on Chemical Safety, Geneva.
Irmak, S., Erbatur, O., and Akgerman, A. (2005). "Degradation of 17beta-estradiol and bisphenol A in aqueous medium by using ozone and ozone/UV techniques." *J Hazard Mater*, 126(1-3), 54-62.

Jensen, K. M., Korte, J. J., Kahl, M. D., Pasha, M. S., and Ankley, G. T. (2001). "Aspects of basic reproductive biology and endocrinology in the fathead minnow (*Pimephales promelas*)." *Comp Biochem Physiol C Toxicol Pharmacol*, 128(1), 127-141.

Jiang, J. Q., Yin, Q., Zhou, J. L., and Pearce, P. (2005). "Occurrence and treatment trials of endocrine disrupting chemicals (EDCs) in wastewaters." *Chemosphere*, 61(4), 544-550.

Jobling, S., Coey, S., Whitmore, J. G., Kime, D. E., Van Look, K. J., McAllister, B. G., Beresford, N., Henshaw, A. C., Brighty, G., Tyler, C. R., and Sumpter, J. P. (2002). "Wild intersex roach (Rutilus rutilus) have reduced fertility." *Biology of reproduction*, 67(2), 515-524.

Jobling, S., and Tyler, C. R. (2003). "Endocrine disruption, parasites and pollutants in wild freshwater fish." *Parasitology*, 126 Suppl, S103-108.

Joss, A., Zabczynski, S., Gobel, A., Hoffmann, B., Loffler, D., McArdell, C. S., Ternes, T. A., Thomsen, A., and Siegrist, H. (2006). "Biological degradation of pharmaceuticals in municipal wastewater treatment: proposing a classification scheme." *Water research*, 40(8), 1686-1696.

Khanal, S. K., Xie, B., Thompson, M. L., Sung, S., Ong, S. K., and Van Leeuwent, J. (2006). "Fate, transport, and biodegradation of natural estrogens in the environment and engineered systems." *Environmental science & technology*, 40(21), 6537-6546.

Kim, I. H., Tanaka, H., Iwasaki, T., Takubo, T., Morioka, T., and Kato, Y. (2008). "Classification of the degradability of 30 pharmaceuticals in water with ozone, UV and H_2O_2." *Water Sci Technol*, 57(2), 195-200.

Kim, S. D., Cho, J., Kim, I. S., Vanderford, B. J., and Snyder, S. A. (2007). "Occurrence and removal of pharmaceuticals and endocrine disruptors in South Korean surface, drinking, and waste waters." *Water Res*, 41(5), 1013-1021.

Kimura, K., Hara, H., and Watanabe, Y. (2007). "Elimination of selected acidic pharmaceuticals from municipal wastewater by an activated sludge system and membrane bioreactors." *Environmental science & technology*, 41(10), 3708-3714.

Kjølholt, J., Nielsen, P., and Stuer-Lauridsen, F. (2003). "Hormonforstyrrende stoffer og lægemidler i spildevand (In Danish), ." *Danish EPA project no. 799*, Cowi A/S.

Kolodziej, E. P., Harter, T., and Sedlak, D. L. (2004). "Dairy wastewater, aquaculture, and spawning fish as sources of steroid hormones in the aquatic environment." *Environmental science & technology*, 38(23), 6377-6384.

Košutić, K., Furač, L., Sipos, L., and Kunst, B. (2005). "Removal of arsenicnext term and pesticides from drinking water by nanofiltration membranes " *Separation and Purification Technology*, 42(2), 137-144.

Kramer, V. J., Miles-Richardson, S., Pierens, S. L., and Giesy, J. P. (1998). "Reproductive impairment and induction of alkaline-labile phosphate, a biomarker of estrogen exposure, in fathead minnows (*Pimephales promelas*) exposed to waterborne 17[beta]-estradiol." *Aquatic Toxicology*, 40(4), 335-360.

Lam, M. W., and Mabury, S. A. (2005). "Photodegradation of the pharmaceuticals atorvastatin, carbamazepine, levofloxacin, and sulfamethoxazole in natural waters." *Aquatic Sciences - Research Across Boundaries*, 67(2), 177-188.

Lam, M. W., Young, C. J., Brain, R. A., Johnson, D. J., Hanson, M. A., Wilson, C. J., Richards, S. M., Solomon, K. R., and Mabury, S. A. (2004). "Aquatic persistence of eight pharmaceuticals in a microcosm study." *Environmental toxicology and chemistry / SETAC*, 23(6), 1431-1440.

Langevin, C. D. (2001). "Simulation of Ground-Water Discharge to Biscayne Bay, Southeastern Florida." *Water-Resources Investigations Report 00-4251*, USGS.

Lau, T. K., Chu, W., and Graham, N. (2005). "The degradation of endocrine disruptor di-n-butyl phthalate by UV irradiation: a photolysis and product study." *Chemosphere*, 60(8), 1045-1053.
Lee, C., Yoon, J., and Von Gunten, U. (2007). "Oxidative degradation of N-nitrosodimethylamine by conventional ozonation and the advanced oxidation process ozone/hydrogen peroxide." *Water research*, 41(3), 581-590.
Lee, J., Park, H., and Yoon, J. (2003). "Ozonation characteristics of bisphenol A in water." *Environ Technol*, 24(2), 241-248.
Lee, K. E., Barber, L. B., Furlong, E. T., Cahill, J. D., Kolpin, D. W., Meyer, M. T., and Zaugg, S. D. (2004). "Presence and distribution of organic wastewater compounds in wastewater, surface, ground, and drinking waters, Minnesota, 2000-02." *Scientific Investigation Report 2004–5138*, USGS.
Lee, Y., Yoon, J., and von Gunten, U. (2005). "Kinetics of the oxidation of phenols and phenolic endocrine disruptors during water treatment with ferrate (Fe(VI))." *Environmental science & technology*, 39(22), 8978-8984.
Lee, Y., Zimmermann, S., and Gunten, U. v. (Year). "Oxidation of micropollutants and removal of phosphate during treatment of municipal wastewaters by ferrate(VI): comparison with ozonation." *5th IWA leading edge conference on water and wastewater technologies*, Zurich, Switzerland.
Lei, H., and Snyder, S. A. (2007). "3D QSPR models for the removal of trace organic contaminants by ozone and free chlorine." *Water research*, 41(18), 4051-4060.
Leonard, L., Croft, A., Childers, D., Mitchell-Bruker, S., Solo-Gabriele, H., and Ross, M. (2006). "Characteristics of surface-water flows in the ridge and slough landscape of Everglades National Park: implications for particulate transport." *Hydrobiologia*, 569, 5-22.
Li, C., and Li, X. Z. (2007). "Degradation of endocrine disrupting chemicals in aqueous solution by interaction of photocatalytic oxidation and ferrate (VI) oxidation." *Water Sci Technol*, 55(1-2), 217-223.
Li, C., Li, X. Z., and Graham, N. (2005). "A study of the preparation and reactivity of potassium ferrate." *Chemosphere*, 61(4), 537-543.
Li, C., Li, X. Z., Graham, N., and Gao, N. Y. (2008). "The aqueous degradation of bisphenol A and steroid estrogens by ferrate." *Water research*, 42(1-2), 109-120.
Linden, K. G., Rosenfeldt, E. J., and Kullman, S. W. (2007). "UV/H2O2 degradation of endocrine-disrupting chemicals in water evaluated via toxicity assays." *Water Sci Technol*, 55(12), 313-319.
Liu, G. F., Ma, J., Qin, Q. D., Li, X. C., and Li, G. B. (2007). "Ozonation of representative endocrine disruptors (EDs) in water." *Huan Jing Ke Xue (in Chinese)*, 28(7), 1466-1471.
Mabey, W., and Mill, T. (1978). "Critical review of hydrolysis of organic compounds in water under environmental conditions." *Journal of Physical and Chemical Reference Data*, 7, 383-415.
MacLatchy, D., Peters, L., Nickle, J., and Van Der Kraak, G. (1997). "Exposure to beta-sitosterol alters the endocrine status of goldfish differently than 17beta-estradiol." *Environmental Toxicology and Chemistry*, 16(9), 1895-1904.
Massachusetts DEP. (2006). "Perchlorate Fact Sheet." Massachusetts Department of Environmental Protection, <http://mass.gov/dep/toxics/pchlorqa.pdf>.
McLean, J., Sims, R., Doucette, W., Caupp, C., and Grenney, W. (1988). "Evaluation of mobility of pesticides in soil using U.S. EPA methodology." *Journal of Environmental Engineering*, 114, 689-703.

McPherson, B. F., and Miller, R. L. (1987). "The vertical attenuation of light in Charlotte Harbor, a shallow,subtropical estuary, south-western Florida." *Estuarine, Coastal and Shelf Science*, 25, 721-737.

Mellanen, P., Petanen, T., Lehtimaki, J., Makela, S., Bylund, G., Holmbom, B., Mannila, E., Oikari, A., and Santti, R. (1996). "Wood-derived estrogens: studies in vitro with breast cancer cell lines and in vivo in trout." *Toxicology and applied pharmacology*, 136(2), 381-388.

Mill, T., and Mabey, W. (1985). "Photochemical transformations. In: Environmental exposure from chemicals." W. Neely and G. Blau, eds., CRC Press, Boca Raton, FL, 175-216.

Moore, D. E., and Zhou, W. (1994). "Photodegradation of sulfamethoxazole: a chemical system capable of monitoring seasonal changes in UVB intensity." *Photochem Photobiol*, 59(5), 497-502.

Morrall, D., McAvoy, D., Schatowitz, B., Inauen, J., Jacob, M., Hauk, A., and Eckhoff, W. (2004). "A field study of triclosan loss rates in river water (Cibolo Creek, TX)." *Chemosphere*, 54(5), 653-660.

Nakada, N., Shinohara, H., Murata, A., Kiri, K., Managaki, S., Sato, N., and Takada, H. (2007). "Removal of selected pharmaceuticals and personal care products (PPCPs) and endocrine-disrupting chemicals (EDCs) during sand filtration and ozonation at a municipal sewage treatment plant." *Water research*, 41(19), 4373-4382.

Neamtu, M., and Frimmel, F. H. (2006). "Photodegradation of endocrine disrupting chemical nonylphenol by simulated solar UV-irradiation." *Science of The Total Environment*, 369(1-3), 295-306.

Nghiem, L. D., Schafer, A. I., and Elimelech, M. (2004). "Removal of natural hormones by nanofiltration membranes: measurement, modeling, and mechanisms." *Environmental science & technology*, 38(6), 1888-1896.

Nicholas, H. B., Jr., Chan, S. S., and Rosenquist, G. L. (1999). "Reevaluation of the determinants of tyrosine sulfation." *Endocrine*, 11(3), 285-292.

Okuda, T., Kobayashi, Y., Nagao, R., Yamashita, N., Tanaka, H., Tanaka, S., Fujii, S., Konishi, C., and Houwa, I. (2008). "Removal efficiency of 66 pharmaceuticals during wastewater treatment process in Japan." *Water Sci Technol*, 57(1), 65-71.

Orlando, E. F., Kolok, A. S., Binzcik, G. A., Gates, J. L., Horton, M. K., Lambright, C. S., Gray, L. E., Jr., Soto, A. M., and Guillette, L. J., Jr. (2004). "Endocrine-disrupting effects of cattle feedlot effluent on an aquatic sentinel species, the fathead minnow." *Environmental health perspectives*, 112(3), 353-358.

Patino, R., Goodbred, S. L., Draugelis-Dale, R., Barry, C. E., Foott, J. S., Wainscott, M. R., Gross, T. S., and Covay, K. J. (2003). "Morphometric and Histopathological Parameters of Gonadal Development in Adult Common Carp from Contaminated and Reference Sites in Lake Mead, Nevada." *Journal of Aquatic Animal Health*, 15(1), 55-68.

Petrovic, M., Sole, M., Lopez de Alda, M. J., and Barcelo, D. (2002). "Endocrine disruptors in sewage treatment plants, receiving river waters, and sediments: integration of chemical analysis and biological effects on feral carp." *Environmental toxicology and chemistry / SETAC*, 21(10), 2146-2156.

Purdom, C. E., Hardiman, P. A., Bye, V. V. J., Eno, N. C., Tyler, C. R., and Sumpter, J. P. (1994). "Estrogenic effects of effluents from sewage treatment works." *Chemistry and Ecology*, 8(4), 275 - 285.

Radjenovic, J., Petrovic, M., and Barcelo, D. (2007). "Analysis of pharmaceuticals in wastewater and removal using a membrane bioreactor." *Anal Bioanal Chem*, 387(4), 1365-1377.

Razak, A. R., Ujang, Z., and Ozaki, H. (2007). "Removal of endocrine disrupting chemicals (EDCs) using low pressure reverse osmosis membrane (LPROM)." *Water Sci Technol*, 56(8), 161-168.

Reiss, R., Mackay, N., Habig, C., and Griffin, J. (2002). "An ecological risk assessment for triclosan in lotic systems following discharge from wastewater treatment plants in the United States." *Environmental toxicology and chemistry / SETAC*, 21(11), 2483-2492.

Rodriguez-Mozaz, S., de Alda, M. J., and Barcelo, D. (2004). "Monitoring of estrogens, pesticides and bisphenol A in natural waters and drinking water treatment plants by solid-phase extraction-liquid chromatography-mass spectrometry." *Journal of chromatography*, 1045(1-2), 85-92.

Rosen, M. R. (2007). "Methods and precautions in sampling for emerging contaminants in water, biota, and sediment." *California Water Environment Association Workshop, San Ramon, CA*.

Rosenfeldt, E. J., and Linden, K. G. (2004). "Degradation of endocrine disrupting chemicals bisphenol A, ethinyl estradiol, and estradiol during UV photolysis and advanced oxidation processes." *Environmental science & technology*, 38(20), 5476-5483.

Samsøe-Petersen, L., Winther-Nielsen, M., and Madsen, T. (2003). "Fate and effects of triclosan." *Danish EPA project no. 861*, DHI Water & Environment

Schafer, A. I., Nghiem, L. D., and Waite, T. D. (2003). "Removal of the natural hormone estrone from aqueous solutions using nanofiltration and reverse osmosis." *Environmental science & technology*, 37(1), 182-188.

Schlenk, D. S., Hinton, D. E., and Woodside, G. W. (2007). "Online methods for evaluating the safety of reclaimed water." *Water Environment Research Foundation Report 01-HHE-4A*.

Schoenfuss, H. L., Levitt, J. T., Van der Kraak, G., and Sorensen, P. W. (2002). "Ten-week exposure to treated sewage discharge has relatively minor, variable effects on reproductive behavior and sperm production in goldfish." *Environmental toxicology and chemistry / SETAC*, 21(10), 2185-2190.

Schwatter, F., Hannich, C. B., Nothe, T., Oehlmann, J., and Fahlenkamp, H. (2007). "Risk assessment for organic trace compounds in wastewater: comparison of conventional and advanced treatment." *Water Sci Technol*, 56(5), 9-13.

Sharma, V. K., Mishra, S. K., and Ray, A. K. (2006). "Kinetic assessment of the potassium ferrate(VI) oxidation of antibacterial drug sulfamethoxazole." *Chemosphere*, 62(1), 128-134.

Shiu, W.-Y., Ma, K.-C., Varhanícková, D., and Mackay, D. (1994). "Chlorophenols and alkylphenols: A review and correlation of environmentally relevant properties and fate in an evaluative environment." *Chemosphere*, 29(6), 1155-1224.

Skadsen, J. M., Rice, B. L., and Meyering, D. J. (2004). "The occurrence and fate of pharmaceuticals, personal care products and endocrine disrupting compounds in a municipal water use cycle: A case study in the City of Ann Arbor." City of Ann Arbor Water Utilities, Fleis & VandenBrink Engineering, Inc.

Snyder, E. M., Snyder, S. A., Kelly, K. L., Gross, T. S., Villeneuve, D. L., Fitzgerald, S. D., Villalobos, S. A., and Giesy, J. P. (2004). "Reproductive responses of common carp (Cyprinus carpio) exposed in cages to influent of the Las Vegas Wash in Lake Mead, Nevada, from late winter to early spring." *Environmental science & technology*, 38(23), 6385-6395.

Snyder, S., Pleus, R., Snyder, E., Hemming, J., and G., B. (2006a). "Toxicological significance of trace endocrine disruptors and pharmaceuticals in water." *21st Annual WateReuse Symposium*.

Snyder, S. A., Adham, S., Redding, A. M., Cannon, F. S., DeCarolis, J., Oppenheimer, J., Wert, E. C., and Yoon, Y. (2007). "Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals." *Desalination*, 202(1-3), 156-181.

Snyder, S. A., Villeneuve, D. L., Snyder, E. M., and Giesy, J. P. (2001). "Identification and quantification of estrogen receptor agonists in wastewater effluents." *Environmental science & technology*, 35(18), 3620-3625.

Snyder, S. A., Wert, E. C., Rexing, D. J., Zegers, R. E., and Drury, D. D. (2006b). "Ozone Oxidation of Endocrine Disruptors and Pharmaceuticals in Surface Water and Wastewater." *Ozone: Science & Engineering*, 28(6), 445-460.

Soliman, M. A., Pedersen, J. A., Park, H., Castaneda-Jimenez, A., Stenstrom, M. K., and Suffet, I. H. (2007). "Human pharmaceuticals, antioxidants, and plasticizers in wastewater treatment plant and water reclamation plant effluents." *Water Environ Res*, 79(2), 156-167.

Stackelberg, P. E., Furlong, E. T., Meyer, M. T., Zaugg, S. D., Henderson, A. K., and Reissman, D. B. (2004). "Persistence of pharmaceutical compounds and other organic wastewater contaminants in a conventional drinking-water-treatment plant." *The Science of the total environment*, 329(1-3), 99-113.

Stackelberg, P. E., Gibs, J., Furlong, E. T., Meyer, M. T., Zaugg, S. D., and Lippincott, R. L. (2007). "Efficiency of conventional drinking-water-treatment processes in removal of pharmaceuticals and other organic compounds." *The Science of the total environment*, 377(2-3), 255-272.

Swartz, C. H., Reddy, S., Benotti, M. J., Yin, H., Barber, L. B., Brownawell, B. J., and Rudel, R. A. (2006). "Steroid estrogens, nonylphenol ethoxylate metabolites, and other wastewater contaminants in groundwater affected by a residential septic system on Cape Cod, MA." *Environmental science & technology*, 40(16), 4894-4902.

Tamagawa, Y., Yamaki, R., Hirai, H., Kawai, S., and Nishida, T. (2006). "Removal of estrogenic activity of natural steroidal hormone estrone by ligninolytic enzymes from white rot fungi." *Chemosphere*, 65(1), 97-101.

Tang, C. Y., Fu, Q. S., Robertson, A. P., Criddle, C. S., and Leckie, J. O. (2006). "Use of reverse osmosis membranes to remove perfluorooctane sulfonate (PFOS) from semiconductor wastewater." *Environmental science & technology*, 40(23), 7343-7349.

Ternes, T. A., Bonerz, M., Herrmann, N., Teiser, B., and Andersen, H. R. (2007). "Irrigation of treated wastewater in Braunschweig, Germany: an option to remove pharmaceuticals and musk fragrances." *Chemosphere*, 66(5), 894-904.

Ternes, T. A., Stumpf, M., Mueller, J., Haberer, K., Wilken, R. D., and Servos, M. (1999). "Behavior and occurrence of estrogens in municipal sewage treatment plants--I. Investigations in Germany, Canada and Brazil." *The Science of the total environment*, 225(1-2), 81-90.

Thomas, P. M., and Foster, G. D. (2005). "Tracking acidic pharmaceuticals, caffeine, and triclosan through the wastewater treatment process." *Environmental toxicology and chemistry / SETAC*, 24(1), 25-30.

Tsujimoto, T. (1999). "Fluvial processes in streams with vegetation." *Journal of Hydraulic Research*, 37, 789 - 803.

Vanderford, B. J., Pearson, R. A., Rexing, D. J., and Snyder, S. A. (2003). "Analysis of endocrine disruptors, pharmaceuticals, and personal care products in water using liquid chromatography/tandem mass spectrometry." *Anal Chem*, 75(22), 6265-6274.

Vieno, N., Tuhkanen, T., and Kronberg, L. (2006). "Removal of pharmaceuticals in drinking water treatment: effect of chemical coagulation." *Environ Technol*, 27(2), 183-192.

Vieno, N., Tuhkanen, T., and Kronberg, L. (2007a). "Elimination of pharmaceuticals in sewage treatment plants in Finland." *Water research*, 41(5), 1001-1012.
Vieno, N. M., Harkki, H., Tuhkanen, T., and Kronberg, L. (2007b). "Occurrence of pharmaceuticals in river water and their elimination in a pilot-scale drinking water treatment plant." *Environmental science & technology*, 41(14), 5077-5084.
Westerhoff, P., Yoon, Y., Snyder, S., and Wert, E. (2005). "Fate of endocrine-disruptor, pharmaceutical, and personal care product chemicals during simulated drinking water treatment processes." *Environmental science & technology*, 39(17), 6649-6663.
WHO. (2002). "Global assessment of the state-of-the-science of endocrine disruptors." *WHO/PCS/EDC/02.2*, T. Damstra, S. Barlow, A. Bergman, R. Kavlock, and G. Van der Kraak, World Health Organization, International Programme on Chemical Safety Geneva, Switzerland.
Wilkin, R. T. (2007). "Metal attenuation processes at mining sites." *EPA/600/R-07/092*, United States Environmental Protection Agency, National Risk Management Research Laboratory, Cincinnati, Ohio. <http://www.epa.gov/ada/download/issue/600R07092.pdf>.
Woodling, J. D., Lopez, E. M., Maldonado, T. A., Norris, D. O., and Vajda, A. M. (2006). "Intersex and other reproductive disruption of fish in wastewater effluent dominated Colorado streams." *Comp Biochem Physiol C Toxicol Pharmacol*, 144(1), 10-15.
Wu, W., Shields, F. D., Bennett, S. J., and Wang, S. S. Y. (2005). "A depth-averaged two-dimensional model for flow, sediment transport, and bed topography in curved channels with riparian vegetation." *Water Resources Research*, 41, W03015.
Xu, B., Gao, N. Y., Rui, M., Wang, H., and Wu, H. H. (2006). "Degradation of endocrine disruptor bisphenol A in drinking water by ozone oxidation." *Huan Jing Ke Xue (in Chinese)*, 27(2), 294-299.
Xu, P., Drewes, J. E., Bellona, C., Amy, G., Kim, T. U., Adam, M., and Heberer, T. (2005). "Rejection of emerging organic micropollutants in nanofiltration-reverse osmosis membrane applications." *Water Environ Res*, 77(1), 40-48.
Ying, G.-G., Yu, X.-Y., and Kookana, R. S. (2007). "Biological degradation of triclocarban and triclosan in a soil under aerobic and anaerobic conditions and comparison with environmental fate modelling." *Environmental Pollution*, 150(3), 300-305.
Ying, G. G., Kookana, R. S., and Dillon, P. (2003). "Sorption and degradation of selected five endocrine disrupting chemicals in aquifer material." *Water research*, 37(15), 3785-3791.
Zhang, Y., and Zhou, J. L. (2005). "Removal of estrone and 17beta-estradiol from water by adsorption." *Water research*, 39(16), 3991-4003.